

**UNITED STATES AIR FORCE
IERA**

**Lead-Free Small Arms Ammunition
Study**

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November 1999

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and Occupational Health Risk Analysis
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Lead-Free Small Arms Ammunition Study Final Report

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1.0 Executive Summary

The Air Education and Training Command (AETC) supported a study to assess the potential human health and environmental implications of utilizing lead-free ammunition for training purposes. This technical report addresses this issue.

The purpose of this project was to determine any previously unrecognized environmental and health risks associated with the use of lead-free training ammunition at Air Force small arms ranges.

The scope of the study was limited to documenting any environmental regulatory and human health problems (if any) expected from use of lead-free ammunition. Specific concerns were the health effects of the products of combustion of lead-free primers, and the environmental and health effects of copper, tungsten, tin and nylon as projectile components.

The approach to the study was to review information available from the literature, collect information from points of contact (POCs) in government and industry, and search relevant Internet sites for toxicological and other health/environmental information associated with lead-free ammunition. The review was conducted within the conceptual framework of risk assessment to include hazard identification, exposure analysis and risk characterization. No technical investigation, involving experimentation, was conducted. Selection of the organizations to communicate with was determined primarily by the POCs provided by the AETC, although a few were added from the networking process. For the most part, these organizations were either commercial manufacturers of lead-free ammunition and ammunition components or DoD organizations interested in replacing the currently used leaded ammunition with the lead-free alternatives.

The selected organizations were U.S. Fish and Wildlife Service; Simunition-SNC; AF Institute for Environment, Safety and Occupational Health Risk Analysis (IERA); U.S. Army, Picatinny Arsenal; U.S. Army Test and Evaluation Command; AFMC Security Forces; Winchester Division, Olin Corporation; Delta Frangible Ammunition; Ideas to Market LP; Army Research Lab Aberdeen Proving Ground; HQ AETC/CEVQ; Los Alamos National Laboratory; Oak Ridge National Laboratory; U.S. Army Center for Health Promotion and Preventive Medicine; Combat Arms Commander, WPAFB; CCI-Blount, Inc; Army Environmental Center; HQ AETC Security Forces; Federal Cartridge Company; Kent Cartridge Company; Federal Bureau of Investigation; Fiocchi of America; and Naval Surface Warfare Center Crane Division.

Findings

Findings from this study may be summarized as:

- Except for the Army policy of not utilizing training ammunition that is different than field ammunition, all reviewed sources supported replacement of the conventional leaded ammunition with lead-free alternatives for training. The lower toxicity (higher

PEL) and lower water solubility of the presented alternatives strongly indicate an expected reduction in human health and ecological risk.

- With the exception of one study (Ref 5), the reviewed sources of information consistently supported the replacement of conventional ammunition with lead-free alternatives that use tungsten in the projectile. The Delta frangible ammunition was mentioned frequently as a good alternative.
- Lead-free primer composition varies widely. Some investigators favored the Winchester primer because it is lead free and heavy metal free.
- All three of the reviewed sources, which addressed the noise associated with lead-free ammunition, reported that the noise was not significantly different from conventional ammunition.

Conclusions

- No evidence was found to nullify the perceived advantages of substituting the currently available lead-free ammunition for the conventional lead-containing ammunition. Because of the known high toxicity of lead, relative to what is known about the toxicity of lead-free alternatives, the alternatives are preferred from a human health and environmental quality viewpoint. This is true for both projectiles and primers.
- There were no product waste components that would be considered Resource Conservation Recovery Act (RCRA) regulated hazardous waste. No regulatory requirements concerning surface water or ground water were identified, nor were regulatory concerns related to air permitting identified. The lead-free ammunition is significantly less toxic to the environment than the currently used lead ammunition types.
- Technology is changing rapidly with respect to lead-free ammunition suitable for AF training purposes (e.g., projectile and primer composition).
- Ammunition manufacturers typically provide very limited information on the composition of primer and propellant composition because of the proprietary nature. Some Material Safety Data Sheets (MSDSs) have a reasonable amount of information but many do not.
- Though preferable to lead, significant data gaps exist on the toxicology of lead-free ammunition components. Human health effects and environmental quality effects have not yet been well studied and documented.
- Being lead-free does not necessarily make small arms ammunition non-toxic but current evidence suggests it is much less toxic than conventional ammunition.
- Ammunition available on the market with lead-free projectiles but utilizing lead compounds in the primer mixture reduces environmental concerns but does not eliminate the exposure to lead at the firing line positions. This is especially true at indoor ranges where ventilation systems must control the dust concentration (containing lead and lead compounds mainly from the primer) to an acceptable level.
- There is not a significant difference in the noise exposure for the lead-free ammunition as compared to traditional ammunition.

Recommendations

Based on the conclusions, it is recommended that the Air Force:

- Use a risk management approach to substitute lead free ammunition for conventional ammunition for training purposes.
 - Identify possible health-related issues associated with alloy metals when used alone and when present in combination with tungsten and other alloy metals. This will identify synergistic effects, if any, resulting from exposure to more than one metal. This would require a more comprehensive toxicological investigation than was possible within the scope of the current study.
 - Conduct baseline industrial hygiene and environmental surveys at selected firing ranges using the replacement ammunition. The surveys should include air sampling for lead (residual from prior use), tungsten and copper for the Winchester ammunition. Also, the decomposition products of carbon monoxide, ammonia and nitrogen dioxide should be monitored. In general, since a variety of ammunition may be used, sampling requirements should be determined on a case-by-case basis from the manufacturer's MSDSs. Swipe sampling for residual lead, ventilation system evaluation, and noise monitoring should be accomplished at indoor ranges. Environmental considerations should include dust control in the bullet trap area and other contaminant pathway factors such as storm water control and extent of lead contamination from prior use of leaded ammunition.
 - Carefully confirm the composition of all lots of replacement ammunition since manufacturers seem to be changing the composition in search of the "optimal."
 - Train instructors and shooters that being lead-free does not remove all concern for exposure to hazardous materials.
- Establish effective communications with other organizations interested in the use of lead-free ammunition.
- Create a database to consolidate knowledge on lead-free ammunition, as it becomes available through literature search, communications with industry and information exchange with government organizations (e.g., DoD, FBI, DoE, etc.).
 - Capture operational lessons learned with respect to human health and environmental implications.
 - Track the manufacturing trends and formulation changes in ammunition with regard to human health and environmental implications.
 - Conduct an extensive literature search on the toxicology of chemicals used in lead-free ammunition. Keep abreast of latest developments in the toxicology of lead-free ammunition components through technical literature and personal contacts with other using organizations.

2.0 Introduction

Air Education and Training Command (AETC) has significant interest in potential environmental and health problems associated with design and operation of small arms firing ranges (Ref 15). The firing of presently available military ammunition creates environmental and health risks at both old and new ranges.

Most problems are rooted in the presence of lead and lead compounds in bullets and priming mixtures used in ammunition. Older ranges using earth backstops, or no backstops in some cases, have a deferred environmental problem because lead contamination in the soil at such ranges eventually must be cleaned up at the time the ranges are closed or transferred.

Active ranges within AETC are not in violation of present environmental regulations concerning hazardous waste, because environmental regulatory agencies have taken the view that the fired ammunition is being used as intended and that no waste is being generated. Recovery of fired bullets and lead fragments from active ranges generally does not constitute waste generation so long as metals are recycled and no waste metals or contaminated soil are disposed of offsite or onsite. However, if ranges are to be closed or transferred, there will probably be a requirement to perform a site soil cleanup under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and corresponding state regulations.

Human lead exposures at open ranges using earth backstops are usually not a concern, and noise protection is adequate by the simple use of earplugs and/or earmuffs. Due to range differences, each range must receive its own health hazards assessment. Newer ranges use bullet containment traps that confine the lead bullets to a smaller area, however, other problems have been created by the bullet breakup when the bullet impacts the metal trap. Also, there may be increased exposure to shooters and range personnel, as well as increased noise exposure at fully or partially enclosed range.

The surest solution to most health and environmental problems is the adoption and use of lead-free training ammunition (15). However, lead-free does not necessarily mean toxic-free. Therefore, the purpose of this project was to determine any previously unrecognized environmental and health risks associated with use of lead-free training ammunition at Air Force small arms ranges. It was important to document any environmental regulatory and human health problems (if any) expected from use of lead-free ammunition. Specific concerns were the health effects of the products of combustion of lead-free primers, and the environmental and health effects of copper, tungsten, tin and nylon as projectile components.

3.0 Lead-Free Ammunition Background

Conventional military small arms ammunition projectiles consist of a copper outer shell with a lead/antimony core material. This lead/antimony material presents a hazard when fired in both indoor and outdoor ranges. Dust and vaporized lead present a severe health risk to those training on indoor ranges. If adequate ventilation is not available this material is inhaled and assimilated into the body. Presently 150 Army Reserve and over 600 National Guard indoor ranges are inoperable due to lead contamination resulting from inadequate ventilation. The loss of these ranges results in added cost to transport personnel to operable ranges and impacts the readiness of the soldier. Outdoor range contamination by the lead/antimony core projectiles presents other problems. High concentrations of the core materials are found in the impact areas or berms. Due to the solubility of the lead, it is dissolved by the ground water and is absorbed into the flora and contaminates the surface water, thus adversely impacting the natural ecosystem. (The Army Green Ammunition Program web site, www.w3.pica.army.mil/greenammo/projects.htm).

Figure 1 shows a schematic of the typical structure and composition of conventional small arms ammunition.

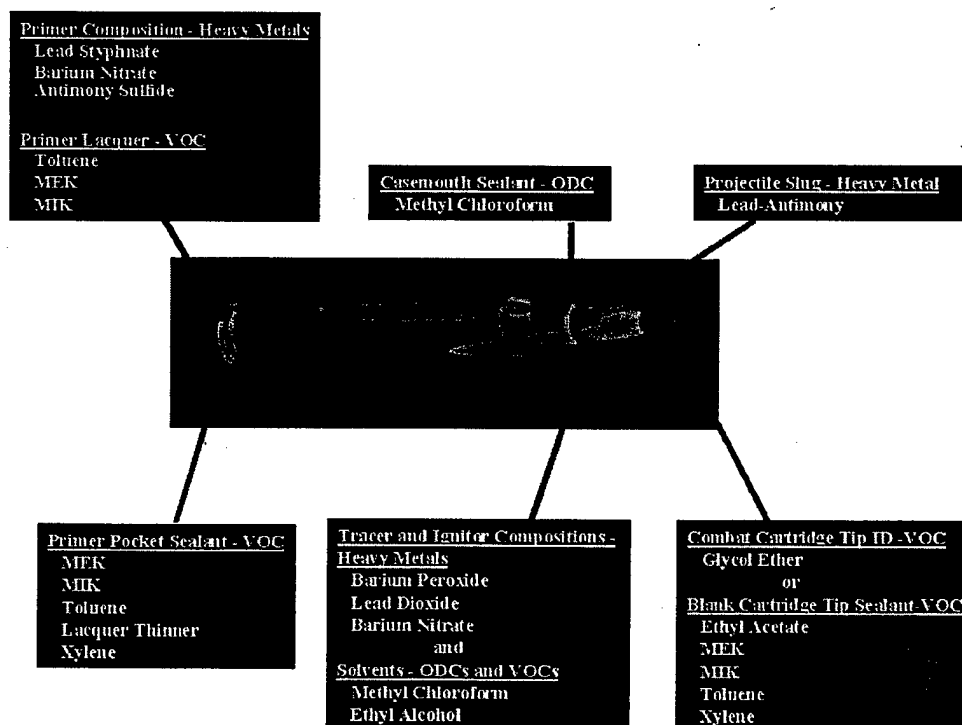


Figure 1. Structure and Composition of Conventional Ammunition, also showing chemicals utilized in manufacturing (www.w3.pica.army.mil/greenammo/projects.htm).

Recent tests have confirmed that lead is a significant environmental and health problem emerging with increasing frequency at many of the public, private, and government operated shooting ranges nationwide. Many of the sites are contaminated with hundreds of tons of lead, the result of years of target practice and skeet shooting. The lead is tainting grounds and water, is being ingested by wildlife and, in extreme cases, has become a serious threat to the health and safety of human and animal populations. Indoor ranges pose other serious concerns such as increased lead exposure to the shooter due to the enclosed space and the subsequent need for high capacity ventilation and air filtration systems. Handling of ammunition and contaminated weapons can also produce elevated lead levels in the blood by absorption through the skin (Ref 6).

Small arms ammunition is comprised of several components (Ref 6); the projectile (the portion of the ammunition which exits the barrel of the firearm), the cartridge case (the portion of the ammunition which acts as a container to hold the projectile, the propellant, and the primer as a single unit), the propellant or powder (the portion of the ammunition which reacts upon firing to produce high pressure gases to propel the projectile from the firearm's barrel), and the primer (the portion of the ammunition which initiates the burning of the propellant material). Each of these components contributes to environmental pollution when the ammunition is expended.

A 1977 study by Juhasz, et.al., examined the relative contributions of the projectile and primer to lead contamination in the uprange and downrange positions (Ref 8). By making selected changes in the test ammunition fired from handguns, it was shown that the uprange aerosol lead contamination could be reduced by a factor of 430 without compromising ballistic performance.

The two possible sources of lead contamination from ammunition are the projectile and the primer. The lead projectile may produce microscopic airborne fragments due to mechanical effects in the barrel and at impact and erosive effects from the propellant gases. The primer mix, generally a composition containing lead styphnate, produces lead-containing decomposition products.

Two areas of concern in the ranges are in the vicinity of the shooter (uprange) and in the impact area (downrange). Lowering uprange contamination would involve reducing or eliminating the lead containing components in the primer and reducing or eliminating the amount of lead torn from the projectile by the barrel rifling and the propellant gases. Reducing downrange lead contamination would probably involve the use of soft targets for lead containing ammunition or the elimination of lead from the projectiles altogether. Copper-jacketed, lead projectiles are commercially available. These may be either partially jacketed, soft point type or a fully jacketed core. A layer of copper protects the base of the projectile, as well as its sides. This type of projectile would prevent formation of lead particles due to the cutting action of the rifling, as well as gas wash at the base of the projectile. The copper fragments that may be formed during the travel of the projectile down the bore or produced upon impact with the target are not nearly as toxic as lead. It should be noted that, with jacketed bullets, there is no bore scrub that would release lead. Most of the lead released from the projectile would result from heat erosion

of the lead core exposed at the bullet base, and this would be the most common scenario involving military small arms ammunition.

Commercial primer explosives are generally mixtures of lead styphnate and barium nitrate (Ref 8). Exact compositional data are not available from the manufacturers. Examination of a table of compositions of military primer mixes, however, provides a general understanding of the situation. The data are presented in Table 1. None of the compositions would be suitable for producing a lead-free primer mix. In the distant past, mercury fulminate had been widely used in many primer compositions. These, however, would not be suitable compositions, since one would be merely substituting one toxic heavy metal for another. During the early 1970's, the Army experimented with some lead-free primer mixes as part of its Caseless Ammunition Program (Ref 8). Several promising compositions were tested. Among these were compositions CP-27 (30% mannitol hexanitrate/70% tetracene); CP-34 (30% diazodinitrophenol/70% tetracene); and CP-35 (40% diazodinitrophenol/60% tetracene). Ultimately, both the Caseless Ammunition Program and these primer projects were terminated, even though test firings by Remington (developer of the primers for the Army) were promising with respect to performance and in reducing indoor range lead concentrations.

This study (Ref 8), using these three primers and copper jacketed projectiles (lead core), demonstrated that a substantial reduction in the aerosol lead contamination from handguns (by a factor of 430) is feasible by making selected changes in the ammunition fired. It was concluded that this improvement should be achievable without sacrificing ballistic performance. The study also demonstrated that it was difficult to get rid of all lead in the samples, even when firing lead-free primers. Conventional cleaning of the barrels that had previously fired conventional ammunition did not remove all lead, and indoor ranges demonstrated a low but measurable background level of lead (Ref. 8).

Table 1. Ingredients of Common Military Priming Compositions (% by weight)

Ingredients	FA70	FA90	PA100	PA101	793	NOL60	NOL130
Lead Styphnate, Basic	--	--	--	53	39	60	40
Lead Styphnate, Normal	--	--	38	--	--	--	--
Barium Nitrate	--	--	39	22	44	25	20
Lead Azide	--	--	--	--	--	--	20
Tetracene	--	--	2	5	2	5	5
Lead Dioxide	--	--	5	--	--	--	--
Calcium Silicide	--	--	11	--	14	--	--
Aluminum Powder	--	--	--	10	--	--	--
Antimony Sulfide	17	12	5	10	--	10	15
Lead Sulphocyanate	25	25	--	--	--	--	--
PETN	--	10	--	--	--	--	--
TNT	5	--	--	--	--	--	--
Potassium Chlorate	52	53	--	--	--	--	--

3.1 Projectile

The ammunition's projectile is the major source of environmental pollution, since the projectile is traditionally composed of lead and/or lead and copper. Both of these

elements are environmental pollutants and health hazards when introduced into the environment in either reacted (evaporated by the heat of firing) or un-reacted (raw metal) forms. Reacted compounds of lead or barium from the ammunition's primer is a second source of pollution from small arms ammunition. The reaction (burning) of the propellant and abrasion of the cartridge case also contribute minor amounts of pollutants.

These issues have prompted the development and evaluation of alternative ammunition that eliminates the undesirable health and environmental aspects of lead. The ammunition must be fully functional and provide characteristics similar to those of "standard issue" analogs to allow personnel to maintain the highest degree proficiency in training, and to meet the many needs for military applications. Recent efforts have focused on metal powders in polymer binders (e.g., tungsten and copper, nylon), plastic or rubber projectiles, and alternate metals such as steel, bismuth or brass. Unfortunately, for some applications, these replacements have yet to meet all established specifications and performance goals (e.g., Army operational field use). However, for other applications, the replacements have performed acceptably. For instance, in most shorter-range training environments, the Winchester-Delta bullets perform fine, every bit as well as ball ammunition.

The concept of environmentally safe or non-toxic ammunition has been explored in the past, but not with the vigor as seen in the last few years. According to Lowden (Ref 6), at the end of WWII, projectiles for 0.30 and 0.50 caliber weapons for training and to replace lead were fabricated from tungsten, iron and Bakelite. More recently, replacement projectiles for training and certification of personnel have been fabricated from tungsten and copper or brass powders in a nylon matrix. The projectiles are formed employing injection-molding techniques and ammunition in different calibers is being marketed by a number of companies. The ammunition is functional and acceptable for many applications; however, the density of some formulations is less than that of the lead components and can cause trajectory and other performance problems.

Another solution is the replacement of lead with other metals such as steel, brass, and bismuth. Steel shot is required for hunting waterfowl in many areas. Due to high hardness and low density, steels are less than desirable choices for use as projectile materials. Bismuth and its alloys have also experienced much popularity as replacements for lead. Bismuth-tin shot is currently available but, again, the density of this alloy is only 86% of that of lead, and this creates concerns with regard to ballistic performance. Steel, bismuth and brass also possess higher hardness and modulus than lead. Another concern with bismuth is the lack of toxicological data. In many categories bismuth has not been evaluated, and is thus not fully accepted as a lead replacement.

The author reported that DoE (Ref 6) has begun the development of rifle and pistol bullets, which are composed of materials that are not significant environmental or health hazards, and which are economically recyclable. It was also desired to develop frangible projectiles that disintegrate upon impact to reduce damage to training facilities, reduce risk when fired in nuclear facilities, and lower the risk of ricochet and personnel injury. For the study, tungsten and tungsten carbide were selected as the high-density component with aluminum, bismuth, tin, and zinc as binders. After some review and study, some

candidate metals were disqualified. Emphasis in this effort was placed on the tungsten-tin composition, a mixture of materials that has performed well in processing studies and preliminary testing. The study found that performance of the bullets with the tungsten-tin stimulant for lead exceeded that of military ball pistol ammunition with a similar bullet weight. It appears that the non-lead bullets can be substituted one-for-one with the lead analogs in small arms (Ref 6).

3.2 Primer

Primer making is the most critical step in ammunition production, requiring extreme quality control to make sure all functions occur properly at the right time. Different chemicals are used in the various mixes, depending somewhat on the end results required, as well as on the choice of the manufacturer. The chemicals can be divided into seven categories as shown in Table 2 for ten different common formulations (Ref 16).

Initiator. The initiator is impact shock sensitive, which allows it to detonate from the firing pin impact. Lead styphnate has for years been the most used initiator for small arms primers.

Sensitizer. The initiator is not quite as impact-sensitive as desired, so a small amount of sensitizer is added to the styphnate to make the mix properly sensitive.

Oxidizer. The oxidizer provides oxygen to burn up the fuel provided so as to supply a satisfactory volume of incandescent gas to light up the powder.

Fuels. These are what the oxygen in the oxidizer burn. They provide a more lasting flame than that produced by the initiators for powder ignition.

Frictionator. Generally not necessary in centerfire primers, but definitely needed in rimfire cartridge cases. The frictionator provides sharp corners against which the particles of sensitizer and initiator are forced by the movement of the primer cup or case rim under the firing pin blow. This assures more positive and rapid compression and rupture of some explosive crystals. It is partly this breaking of crystal, which starts the primer action.

Binders. In most primers, the mix is not self-adherent when dry, and some sort of binder must be used to hold the mix in place. Various gums, starches and similar materials may be used.

Other Materials. Certain other materials have been used in some priming mixes (e.g., coloring). Also, some use is also made of pentaerythritoltetranitrate (PETN), as well as TNT and, occasionally, diazodinitrophenol (DDNP). The function of these materials in the primer is not so much as an explosive as it is a source of heat and energy, except that DDNP is also a sensitive initiator. Some use is also made of nitrocellulose in finely divided form for the same purpose.

Table 2. Common Priming Mixes (Ref. 16)

Function	Chemical	I	II	III	IV	V	VI	VII	VIII	IX	X
Initiator	Lead Styphnate	40	45	40	37	37	38	40	40	45	36
Sensitizer	Tetracene	2	4	2	4	4	2	4	4	3	3
Oxidizers	Barium Nitrate	30	22	-	30	32	39	30	34	42	40
	Lead Nitrate	-	-	30	-	-	-	-	-	-	-
	Lead Peroxide	-	7	-	-	-	5	-	-	-	-

Fuels	Antimony Sulfide	-	-	-	25	15	5	16	16	-	11
	Lead Sulfo cyanate	8	-	8	-	-	-	-	-	-	-
	Calcium Silicide	-	-	-	-	-	11	-	-	-	10
	Aluminum	-	-	-	4	7	-	5	-	-	-
Frictionator	Ground Glass	20	22	20	-	-	-	-	-	7	-
Others	PETN	-	-	-	-	5	-	5	6	3	-

Juhasz and Bullock (Ref 13) completed a feasibility study on an environmentally friendly, lead-free primer. Initial ballistic tests of an experimental lead-free primer composition for small arms, capable of functioning under cold, ambient, and hot conditions was described. Experimental primer assemblies using a proprietary primer mix based on boron chemistry were loaded into standard military 9-mm cartridges and tested over a wide operational temperature range. Chamber pressure and muzzle velocity data were compared with conventional reference standards. The test rounds using the lead-free formulation functioned well at all temperatures. The data represented a proof-of-principle of an environmentally friendly, lead-free primer chemistry capable of meeting military extreme cold and hot temperature operating requirements.

As mentioned above, the explosive primer mix currently in use contains lead styphnate, barium nitrate, and antimony sulfide as major constituents. All three are toxic heavy metals. Commercial non-toxic primers are available but will not meet the operating temperatures required for military ammunition. Additionally, shelf life of these primers is limited. The DoD Strategic Environmental Research and Development Program (SERDP) program addresses the primer development. The DoE's Los Alamos National Laboratory has been conducting early experimentation on Metastable Intermolecular Composites, which may have direct application to small caliber primer technology. DoE has funded early exploration of this emerging technology as a replacement for high explosive compounds. The SERDP program is leveraging from this effort and initial testing has been successful (www.w3.pica.army.mil/greenammo/projects.htm).

Information on other lead-free percussion primer mixes based on metastable interstitial composite (MIC) technology was reviewed (Ref 21). It could not be determined if this was the same as the Los Alamos work but, certainly, the technology was similar if not the same. In this case, the component consisted of a lead-free percussion primer composition and a percussion cup containing the composition. The lead-free percussion primer composition is comprised of a mixture of about 45% (by weight) aluminum powder having an outer coating of aluminum oxide and molybdenum trioxide powder or a mixture of about 50% aluminum powder having an outer coating of aluminum oxide and polytetrafluoroethylene (Teflon) powder. The aluminum powder, molybdenum trioxide powder and Teflon powder have a particle size of 0.1µm or less. The percussion primer compositions of this invention, unlike the commonly used lead-based explosive compositions that detonate, react together under mechanical impact, causing an extremely intense exothermic reaction, similar to the Thermite reaction between aluminum powder and iron oxide. This reaction liberates a great amount of heat and burning particles, which causes the main charge of propellant in the ammunition to ignite and rapidly burn. The by-product of the reaction of aluminum and molybdenum trioxide consists of

alumina (a ceramic) and molybdenum, both being relatively non-toxic and environmentally benign. Also, it was reported that the MIC materials met the performance requirements of military ammunition, including low temperature operations. It should be noted, however, that MIC technology appears to be in the pre-development stage and that operational feasibility is five to ten years into the future.

3.3 DoD Policy to Implement EPA's Military Munitions Rule

Whatever the particular composition of the lead-free ammunition, it is important that its management be compliant with the military munitions rule.

Over the years, Congress has specifically delegated statutory authority to the Department of Defense (DoD) for developing and promulgating explosives safety regulations for the safe storage, handling, and use of munitions. DoD has demonstrated a long and successful history in the management of these hazardous materials. The Resource Conservation and Recovery Act (RCRA) of 1976 established specific regulations for the determination of when an item becomes waste, and how hazardous waste items are to be managed. In 1992, the Federal Facility Compliance Act (FFCA) was signed into law. This law required the U.S. Environmental Protection Agency (EPA), in consultation with DoD and the States, to publish regulations that identify when conventional and chemical military munitions become hazardous waste and subject to Subtitle C of RCRA, and that provide for the safe storage and transportation of such waste. These regulations, entitled the Military Munitions Rule (MR) (62 FR 6621, February 12, 1997), that define when military munitions become waste and how these waste military munitions (WMM) will be managed, became effective at the Federal level on August 12, 1997 (Ref 17). The MR defines special requirements for the management of WMM that differ from how other wastes are managed under the RCRA regulations that govern the management of hazardous waste. As a Federal regulation, it establishes a minimum standard for the management of WMM in the United States and U.S. Trust Territories.

Under RCRA, EPA may authorize a State or Territory, instead of the Federal government, to administer and enforce RCRA. While the regulations adopted by a State or Territory have to be at least as stringent as the Federal regulations, RCRA allows States and Territories to impose standards that are more stringent than those in the Federal program. Therefore, compliance requirements may differ from State to State or Territory. Installation or responsible activity commanders should contact the applicable DoD Component Regional Environmental Coordinators (REC) office to determine what specific compliance requirements apply.

This reviewed DoD policy document interprets the requirements of the Military Munitions Rule (MR) (62 FR 6621, February 12, 1997) and establishes an overarching policy for the management of waste military munitions (WMM) that is consistent among DoD Components.

The definitions of when military munitions become WMM (Chapters 4 and 5 of the policy document) and the Designated Disposition Authority (DDA) Evaluation Process

(Chapter 6 of the policy document) apply at all activities effective immediately. These requirements are not dependent upon a State or Territory's adoption of the Federal MR or adoption of other State or Territory standards. Appendix M presents the decision-making process for determining when a WMM becomes a hazardous waste under RCRA (e.g., it presents Chapter 6 and Figure 1 from the policy document).

4.0 Lead-Free Ammunition Risk Findings

The review was conducted within a risk assessment conceptual framework. The risk management associated with the use of lead-free ammunition should consider hazard identification (e.g., bioeffects of an agent and dose response), exposure analysis (e.g., pathways to a receptor organism and likelihood of exposure occurring) and risk characterization (e.g., expression of outcome such as an illness incidence rate, etc.). Operationally, the exposure analyses and risk characterizations are scenario dependent and are addressed here primarily in terms of cited exposure studies. Most emphasis, primarily because of availability of information, focuses on the hazard identification aspect.

4.1 Hazard Identification

Hazard identification deals with the bioeffects of an agent upon a chosen subject (e.g., what is the response given that an exposure occurs), to include dose-response information. In this study, the agents of concern are the toxic chemicals making up the lead-free alternatives to leaded ammunition and the noise associated with the firing of weapons. Even though the toxicity of most of the lead-free alternatives appears to be less toxic than lead, they still demonstrate a level of toxicity and need to be managed with good industrial hygiene practices. Fortunately, in many cases, operational exposure levels have been established that take into account the existing toxicity information. This section will address the toxicity of materials found in the lead-free ammunition and the noise exposure information available for review.

4.1.1 Toxicity

Tungsten appears to be a leading ingredient for the manufacturing of lead-free projectiles. With respect to tungsten toxicity, there are relatively few studies dealing specifically with the effects of tungsten alone, i.e., in the absence of other complicating metals in respirable dust (Ref 12). The deposition of tungsten and alloy metals in the body is dependent on a number of factors: chemical form, concentration, and solubility of the compound in body fluids, particle size, and route of entry. Because tungsten itself is relatively inert, the physiological effects that are manifested in response to an alloy are dependent primarily on the binding agents present. For example, concerning interstitial pulmonary fibrosis, the cementing agent cobalt, in association with tungsten carbide, was identified as the probable causative agent. With respect to tungsten toxicity, the following was noted in this review.

- Tungsten competes with molybdenum in metabolic processes, having an effect on several enzyme systems where it interferes with the role of molybdate, e.g., xanthine dehydrogenase, sulfite oxidase, aldehyde oxidase, and nitrate reductase. It is hypothesized that tungsten occupies sites on the enzymes where normally molybdate would be present.
- The antagonistic effect of tungsten on the molybdenum content of rat liver was studied in relationship to estrogens and mammary cancer in experimental rats. That investigation was initiated as a result of high incidence of breast cancer mortality in men and women from a province in China where tungsten is mined. This is reportedly an ongoing project and, to date, no information regarding the residents' uptake of tungsten from food or water had been collected.
- Tungsten is regarded as being moderately toxic, a probable oral lethal dose to humans being between 0.5 and 5.0 g/kg, e.g., roughly somewhere between an ounce and a pound for a 150 lb individual. It is noteworthy; however, that in one instance powdered tungsten metal was provided orally for radiological testing as a substitute for barium. No ill effects on the patient were reported from a dose of 25 to 80 gm according to the Registry of Toxic Effects of Chemical Substances.
- Data reported in the Registry of Toxic Effects of Chemical Substances identify reproductive effects on rats exposed orally to tungsten; there are no reports of effects on human reproduction. Furthermore, insoluble tungsten-containing compounds have not been reported to be mutagenic, carcinogenic, or teratogenic in humans.

Another reviewed study was not supportive of the use of tungsten. SAA International LTD (Ref 5) conducted an information search of toxic-free ammunition for the U.S. Army ARDEC in 1994. The investigators stated objective was to look at the different materials that are generally used in ammunition components, and to focus on their relative toxicity. They reported that this resulted in some controversy since several organizations had already reached conclusions and have been designing ammunition that was supposed to be toxic-free. The problem may be that lead-free and toxic-free may have been taken to mean the same thing. Several organizations had focused on tungsten as a substitute for lead and the small arms community had showed very little concern for the potential toxic effects of tungsten. The investigators then paid more attention to tungsten and other heavy metals to be sure that the Army was not being led into making a substitution where the new material is not thought of as being toxic only because it has not yet been proliferated. Bismuth and molybdenum were given as other examples of such candidate materials.

According to the authors, tungsten is probably the most controversial of the heavy metals from the point of view of its toxicity. This is unusual because it has been used in industry and in consumer products for many years, and there is a great deal of data on its effects. Tungsten has been used as an ammunition component in armor-piercing rounds of all calibers, and several companies have made bullets of frangible tungsten, which is a tungsten alloy powder round in a plastic matrix. The express purpose of several of these rounds has been as a non-toxic training substitute for lead service cartridges. The authors (Ref 5) stated that it is in this powdered form that it is an insidious toxin, and may actually be more dangerous than lead. Tungsten is most commonly used in the hard

metal industry, as a component of cutting tools, and this is where much data has been gathered.

They reported that tungsten, in its unalloyed, insoluble form, causes transient or permanent lung damage and skin irritation. Occupational exposure to mixed tungsten dusts result in exertional dyspnea, coughing, weight loss, extrinsic asthma, pneumonitis, fibrosis, headaches, dizziness, nausea, and loss of the sense of smell. Tests in laboratory animals have resulted in epileptic-like seizures. Unlike lead, tungsten is deposited in the bone tissue and cannot be excreted by the body. It has also been observed that breast cancer mortalities among the residents to tungsten mining areas in China, where over one half of the world's tungsten production is mined, are markedly higher than the national average.

The authors argued that the NIOSH TWA exposure limit for tungsten depends on the alloyed form. For pure insoluble tungsten this limit is 5mg/m^3 , however, when tungsten is alloyed with 3% nickel, it goes down to 0.015 mg/m^3 . Although tungsten has been an important industrial metal for many years, there seems to be a dearth of quantitative data that can be used to assess the effects of the alloys for interest. Much of the available data is not consistent. According to them, it is clear that tungsten is a highly toxic substance, and its use in any situation where dust will be produced must be measured very carefully. Due to its potential use in frangible training ammunition, it is important to understand the potential danger to proliferating tungsten ammunition, and to monitor its use very carefully.

It is interesting to note that the conclusions and recommendations in this report (Ref 5) did not favor the tungsten as a substitute for lead. They recommended:

- The simplest modification is to simply substitute bismuth and/or molybdenum for the lead, using the current M59 design as a baseline, with no jacket modifications. For reference, the M59 is equivalent to the 7.62mm ball M80 with most of the lead core replaced with a mild steel core.
- The next level of design complexity is to develop a copper-based M59 derivative projectile in either pure copper (jacket material) or copper-jacketed brass or bronzes as terminal ballistics require.
- They concluded that the highest payoff is to develop a copper jacketed all steel (deemed non-toxic) core bullet, which would need an increased muzzle velocity to compensate for trajectory drop.

In other work, the efforts by the U.S. Fish and Wildlife Service (FWS) was very useful in the review because it presented extensive toxicity data. Over the last several years, the FWS conducted extensive review of candidate replacements for lead shot used in migratory bird hunting (Refs 10 and 11). Extracts from the Federal Register are shown in Appendix A and summarize extensive toxicity test results regarding expected risk to birds and other wildlife. The agency approved several alternative shot as being significantly less toxic and presenting less risk than lead shot. These approved alternatives included (Note: some approvals were temporary, demanding more test data to become permanent): tungsten iron, tungsten-polymer, tungsten-matrix, tin, and bismuth-tin. Table 3 presents a

summary of toxicological information for tungsten and other components in lead-free projectiles.

Table 3. Summary of Toxic Hazards for Lead-Free Projectile Ingredients.

<u>Ingredient</u>	<u>CAS Number</u>	<u>Exposure Limit</u>	<u>Toxicity Comment</u>
Tungsten Powder	7440-33-7	5 mg/m ³ TLV 10 mg/m ³ STEL	Moderately Toxic See Appendix B (Insoluble) See Appendix C (Soluble Compounds)
Tungsten Carbide	12070-12-1	PEL: 5 mg/m ³ W TLV: 5 mg/m ³	See Appendix B
Copper Powder	744-50-8	1 mg/m ³ (dust) 0.2 mg/m ³ (fume) TLV	See Appendix C
Nylon 6/9	27136-65-8	NA	No Reported Toxic Effects (rated no health hazard)
Zinc Stearate	557-05-1	10 mg/m ³ TLV	See Appendix F
Bismuth	7440-69-9		Low Toxicity
Molybdenum	7439-98-7	PEL: 10 PPM TLV: 10 PPM	
Brass			Alloy of high toxicity due to lead and Nickel
Steel			Alloys -Slight Health Hazard
Tin	7440-31-5	PEL: 2 mg/m ³	Low Health Hazard
Iron	07439-89-6	PEL: 10 mg/m ³ (Dust) TLV: 5 mg/m ³ (Dust)	Slight Health Hazard

Now that the toxicity of projectile components has been reviewed, the toxic hazard associated with lead-free primer ingredients will be considered. Table 4 presents a summary of observed toxicity information for materials that may be components in lead-free primers. Note that ammunition from different manufacturers have different combinations of the shown ingredients. When possible, more detailed toxicity information is presented in the appendices as referenced in the table.

Table 4. Summary of Toxic Hazards for Lead-Free Primer Ingredients.

<u>Ingredient</u>	<u>CAS Number</u>	<u>Exposure Limit</u>	<u>Toxicity Comment</u>
Copper	7440-50-8	1 mg/m ³	See Appendix D
Zinc	7440-66-6	5 mg/m ³ (Resp.Dust)	See Appendix F

Diazodinitrophenol (DDNP)	4682-03-5	NA	
Nitrocellulose	9004-20-0	NA	
Barium Nitrate	10022-31-8	0.05 mg/m ³	
Tetracene	109-27-3	NA	
Nickel	7440-02-2	1 mg/m ³	See Appendix E
Nitroglycerin	5563-0	0.2 PPM Ceiling, 0.05 PPM (TLV)	
Potassium Nitrate	7757-79-1	NA	LD50(ORAL-RAT):3750MG/KG
Boron Metal	7440-42-8	15 mg/m ³ Total Dust & 5 mg/m ³ Respirable (PEL)	Exposure Std. As boron Oxide Toxic by inhalation, ingestion and through skin absorption. Irritant. May cause CNS disturbances. ORAL-RAT LD50 650 mg/kg.
Aluminum Powder	7429-90-5	PEL: 15 mg/m ³ Dust, TLV: 10 mg/m ³ Dust	Slight Health Hazard
Antimony sulfide	1345-04-6		Moderate Health Hazard
Molybdenum Trioxide Powder	1313-27-5	(PEL): 15 mg/m ³ , TLV: 10 mg/m ³	Moderate Health Hazard
Tetrafluoroethylene Powder (Teflon)	116-14-3		Mild CNS depression upon exposure to high concentrations. Eye and respiratory irritant. Acute IHL-RAT LC50 40000 ppm

4.1.2 Noise

The Federal Occupational Safety and Health Administration (OSHA) publishes the Permissible Exposure Limit (PEL) for determining employee noise exposures and for complying with OSHA's Hearing Conservation Amendment to the Occupational Noise Exposure regulation. The OSHA PEL for an eight-hour Time Weighted Average (TWA) is 90 decibels (dBA). Generally, this is the maximum noise level that employees may be exposed to without hearing protection during an eight-hour workshift. Table 5 lists additional OSHA noise PELs that are based on the eight-hour, TWA PEL of 90 dBA (www.osha-slc.gov/dts/osta/otm/otmiii/otmiii5.html).

In addition, OSHA requires implementation of noise exposure controls at exposures at or above the OSHA eight-hour TWA action limit of 85 dBA. Exposure controls include participation in a Hearing Conservation Program, including audiometric testing and training. Furthermore, OSHA requires that the employee be offered hearing protection.

Table 5. OSHA Noise Permissible Exposure Limits

Duration Per Day (hours)*	Sound Level (dBA)
8	90
6	92
4	95
3	97
2	100
1.5	102
1	105
0.5	110
0.25	115

*Maximum allowable exposure time (without hearing protection) at given noise level.

4.2 Exposure Considerations

During exposure analysis, consideration is given to ways people might be exposed to the chemicals (or other agent) of concern and at what levels. Risk assessors also figure out over how many years this exposure might reasonably be expected to occur. People may come into contact with chemicals in a variety of ways: breathing, touching, or consuming contaminated air, water, soil, or food. For each of these "pathways," estimates are made of quantities of a given chemical that could reach a person's lungs, digestive system, or skin.

EPA human health risk assessment guidance for Superfund sites consists of having risk assessors calculate the "Reasonable Maximum Exposure" scenario, or RME. The RME portrays the highest level of human exposure that could reasonably be expected to occur from the chemicals identified. Exposures are calculated for groups of people like children, site workers, and residents. They take into account how long, how often, and how many ways people could be exposed to site chemicals. The RME scenario also factors in the number of years exposure could occur if the site were not cleaned up. Both current and likely future uses for the site are considered. This step helps ensure the selected cleanup remedy protects all people around a site, with a focus on the most vulnerable or sensitive populations. It should be noted that the basic systems approach embodied in this guidance is applicable to the problem solving required at any contaminated site, not just Superfund.

Risk assessors use two methods to evaluate the human health effects arising from exposure to Superfund site contaminants. One approach calculates the chance of cancer occurring as a result of exposure. The other compares what is known about the non-cancer health effects of chemicals to the concentration of those chemicals at the site. The likelihood of any kind of cancer resulting from a Superfund site is expressed as a probability; for example, a "1 in 10,000 chance." In other words, for every 10,000 people that could be exposed, one extra cancer case may occur as a result of exposure to site contaminants. An extra cancer case means that one more person could get cancer than would normally be expected to from all other causes. Non-cancer health effects can range from rashes, eye irritation, and breathing difficulties to organ damage, birth defects, and death. Risk assessors calculate a "hazard index" for non-cancer health effects. The key concept here is that a "threshold level" (measured usually as a hazard index of less than

1) exists below which non-cancer health effects are no longer predicted. Risk assessors determine the amount of a chemical that can cause a noticeable non-cancer health effect. Then they use the data to figure out how dangerous the site contaminants are. These methodologies provide an appropriate framework for accomplishing the decision making with respect to the lead-free ammunition exposure issues.

In addition to human health risk assessment, ecological risk from firing ranges needs to be considered as part of the total process.

4.2.1 Environmental Quality

Environmental Assessment of the Delta frangible ammunition MSDSs was accomplished (Ref 3). The MSDSs provide information necessary to assess the environmental and health concerns associated with the ammunition. The MSDSs for the Delta frangible ammunition (DFA) bullets (used by Winchester) were assessed by the Lockheed Martin Energy Systems, K-25 Site Environmental Management Division and by the EG&G, Rocky Flats Environmental Office in accordance with federal regulations pertaining to Resource Conservation and Recovery Act (RCRA), Clean Air Act (CAA), and surface and ground water, and Tennessee and Colorado environmental regulations. From this assessment it was determined that:

- MSDSs do not list any characteristic hazardous waste that presents a RCRA concern;
- The projectile components are not listed as hazardous air pollutants or known carcinogens, thus there is no unusual air permitting requirement; and
- The main components of the projectiles, (i.e., tungsten, copper, and plastic), are environmentally preferable (from both surface and ground water standpoint) because they are less toxic than lead.

The materials do not bioaccumulate in aquatic life as readily as lead and are much less likely to travel through the food chain.

Environmental assessments (Ref 3) of the ammunition MSDSs revealed no product waste components that would be considered RCRA regulated hazardous waste. No regulatory requirements concerning surface water or ground water were identified. In addition, no regulatory concerns related to air permitting, as well as no associated concerns with carcinogens were identified. The ammunition types evaluated were found to be significantly less toxic to the environment than the currently used lead ammunition types. DoE concluded that adoption of the DFA would: reduce cost to DoE controlled indoor ranges currently handling and managing RCRA waste and establish new waste minimization programs in many range areas; reduce or eliminate lead projectiles being placed into the environment by current range operation.

An Army study on tungsten alloy penetrators (Ref 12) addressed environmental effects. The reviewer concluded that no environmental hazard is posed by either tungsten or its compounds. Some environmental contamination with tungsten is known to occur on a limited scale as a result of mining, milling, processing, and industrial applications. There were no definitive reports of associated toxicity of other health effects. Only one study

alluding to possible effects of tungsten toxicity on humans resulting from these operations came to their attention. The study pertained to a high incidence of mortality from mammary cancer among people living in a region where tungsten is mined.

In a manner similar to tungsten alloy penetrators, it is conceivable that tungsten-containing small arms projectiles could create suspended particles in the target area upon impact. The concentration in air is immediately affected by several factors: fragment and dust size distribution, wind speed, precipitation, and other atmospheric conditions. In the penetrator study, it was reported that tungsten oxide particles must be under 20 μ aerodynamic equivalent diameter (AED) to be carried significant distance downwind, and to be less than 10 μ AED (a conservative estimate of the respirable size fraction) to be an inhalation hazard. None of the available reference material provided particle size distributions for the dust associated with projectile impact, though a limited analysis (Ref 7) indicated numerous small particles having diameters less than 0.64 μ , and another study (Ref 20) presented collections of large fragments. Also, the effect of the nylon matrix upon respiratory hazard was not addressed in the available references. A significant data gap appears to exist in this area.

Regarding soils and water contamination (Ref 12):

- Based on a simulation of tungsten deposited in two different environments (wet or arid) in the top 15 cm of soil, it was concluded that, in an arid environment, the difference in concentration after deposition will not change very much between one and 100 years. At a wet site after 100 years, however, there would be a substantial reduction in residual tungsten. In other words, there is greater potential for migration of the metal into the surrounding ecosystem at a wet site than at an arid one.
- Tungsten (added as tungstic acid at a concentration of 50 μ g tungsten/gram of soil) had a sterilizing effect on the soil. Tungsten affected trace metal uptake in a number of ways and, like cobalt, decreased the uptake of other heavy metals. Physical, chemical and biological conversion processes for tungsten alloy oxides at test sites are not known. This data and experimental plant uptake data are needed to evaluate the effects of tungsten alloy metals on plant productivity.
- Tungsten is a constituent of enzyme systems in some species of bacteria.
- Sodium tungstate is not broadly toxic to insect species. It does affect termites, however, perhaps due to the effect on the bacterial flora present in the gut of the termite.
- Tungsten was evaluated along with other metals by the EPA and judged to have low toxicity to algae and aquatic crustaceans; no information was found that implicated tungsten toxicity toward birds. In a comparison of relative metal toxicities, the EPA reported that tungsten was sufficiently less toxic than lead to algae and daphnia (and to laboratory rats), to warrant using tungsten as a substitute for lead.

Work in progress at Oak Ridge National Laboratory (telecommunications with Richard Lowden at ORNL and Wade Bunting at ARDEC) is addressing the leaching of tungsten in soil/water mixtures. It is also addressing movement of tungsten into the food chain via earthworm uptake. From a briefing given to the Tri Service Small Arms Lead-Free

Ammunition Working Group in July 99 by Mr. Lowden (Ref 14), the following points were made regarding this work.

- The widespread distribution of tungsten powder into the environment has not been considered in earlier studies.
- Tungsten can and will be leached into the environment under certain conditions.
- Tungsten was stable in mixture of soil and water (no leaching).
- Corrosion of tungsten is affected by the presence of the other metals, e.g., iron, copper and tin.
- The impact of tungsten leached from ranges to the environment is not fully known.
- Plant and worm studies are being conducted to assess biological uptake of tungsten from bullets fired at shooting ranges. Preliminary earthworm studies showed no tungsten uptake.

4.2.2 Industrial Hygiene

4.2.2.1 Exposure to Toxic Chemicals. An Army test (Ref 1) conducted a "toxic fumes" test. The objective was to determine the toxic gas concentrations and heavy-metals levels produced by the frangible training ammunition when fired from various service weapons. The criterion was the 5.56- and 9-mm frangible training ammunition will produce toxic gas concentrations equal to or less than those levels produced by standard ball ammunition. Personnel shall not be exposed to heavy metal levels in excess of the most stringent limits established by the OSHA. The test was done IAW Army protocol. The weapon to be fired was placed in a test fixture enclosed in a sealed toxic fume chamber. All firing was done remotely. Each type of ammunition was fired to obtain five valid trials from the appropriate weapons. The toxic fume and heavy metal concentrations were recorded during and after the firing of the weapon until the concentrations had declined to an acceptable level. A circulating fan installed in the chamber homogenized the chamber air and was assumed to create uniform concentrations throughout the chamber volume. During all firing trials, the air inside the small test chamber was continuously monitored for carbon monoxide (CO), ammonia (NH₃), nitric oxide (NO), nitrogen dioxide (NO₂), sulfur dioxide (SO₂) and carbon dioxide (CO₂). The results of the tests are summarized in Tables 6 and 7.

Table 6. Toxic Gas Concentrations.

	Ammunition		No. of Trials	Firing Time, Sec	Mean Steady-State Concentration, ppm		
Weapon	Caliber	Type			CO	NH ₃	NO
M16A1	5.56-mm	Frangible	5	2	998	11	11
		Ball	5	2	1112	11	7
GUU5P		Frangible	5	2	766	7	4
		Ball	5	2	812	11	3
M9	9-mm	Frangible	5	28	1270	<6	34
		Ball	5	25	1310	<6	26
MP5		Frangible	^a 3	2	1977	13	84
		Ball	5	2	1862	6	55

^aThe cardboard panel came loose during the first two trials, allowing gases to escape. These trials were declared No-Test.

Technical analysis of the results indicates that the 5.56-mm frangible ammunition produced lower levels of CO gas than the standard ball ammunition. The test ammunition produced slightly higher concentrations of NO gas and near equivalent levels of NH₃. Concentrations of the remaining gases were below the detectable limits for the test instrumentation. With reference to Table 7, it was noted that the low lead concentrations for the frangible test ammunition, which was lead free, was likely due to the residue that was not completely removed from the toxic fumes chamber or the weapons. The investigators concluded that the test criterion was met.

Table 7. Lead Concentrations.

	Ammunition		Time, min	Lead Concentration mg/m ³
Weapon	Caliber	Type		
M16A1	5.56-mm	Frangible	25	0.04
		Ball	25	0.65
GUU5P		Frangible	25	0.004
		Ball	25	0.643
M9	9-mm	Frangible	25	0.151
		Ball	25	9.36
MP5		Frangible	25	0.10
		Ball	25	9.65

In another effort, the Army Armament Research Development and Engineering Center (ARDEC) performed various tests on samples of 9-mm lead free primer ammunition from SNC, Inc. and Dynamit Nobel (Ref 4). Three primers were tested: CCI, Fiocchi, and Dynamit Nobel that are all commercially available. A variety of performance tests were performed and, also, the primers were subjected to various analytic techniques to

identify constituent materials and products of combustion (important for toxic hazard identification).

The toxic fumes test was conducted using an M9 pistol mounted in a Ransom rest. The test support weapon was placed in a test stand enclosed in a sealed toxic fumes chamber with the muzzle of the weapon inside the chamber. During firing, the air inside the chamber was continuously monitored for carbon monoxide (CO), ammonia (NH₃), nitrogen dioxide (NO₂), nitric oxide (NO) and sulfur dioxide (SO₂). Gas samples were collected and analyzed to determine if any relatively high molecular weight gases were produced during firing. Lead samples were collected using a procedure based on NIOSH Method 7300. All firings were conducted remotely using a lanyard.

The toxic fumes tests were conducted by comparing data for U.S. 9-mm M882 ball ammunition and the three lots of lead free test ammunition. The results indicated that the levels of CO for the test ammunition were below those of the M882 ammunition, ranging from 1.4% to 40% lower. In addition, the levels of NO for the test ammunition were 4% to 24% lower than the standard 9-mm cartridge. The levels for NO₂, SO₂ and NH₃ were below the detection limits of the analyzer for the ammunition tested. The mean levels for CO and NO were compared. For CO, the mean for lot SNC/Fiocchi (840 ppm) was significantly lower than means for lots Dynamit (1380 PPM) and the reference M882 ball ammunition (1400 PPM). For NO, the mean of lot Dynamit (19 PPM) was significantly lower than all other lots (ranging 24-27 ppm). No other significant differences were detected. Lead was detected for the control ammunition, as well as the three samples of test ammunition. However, the levels decreased as the ammunition was fired and there was a dramatic decrease from the control ammunition to test ammunitions. Based on the fact that there was a very small percentage of lead detected in the primer mixture analysis, it is hypothesized that the lead levels detected during the toxic fumes test were based more on residual lead left in the chamber from the control ammunition.

A primer chemical analysis was performed. Analyzed chemicals were tetracene, diazodinitrophenol, lead, barium, antimony, strontium, zinc and titanium. The tests indicated that there is significantly less lead in the three test primers when compared to the standard 9-mm ammunition. With the following exceptions, the detected metals were less than 0.0073% of the primer mix. Antimony was 1.95% in the Fiocchi primer. Strontium was 0.52% in the CCI primer. Zinc was 19.98%, 0.11% and 0.12% for the Dynamit, Fiocchi and CCI primer, respectively. Titanium was 0.11%, 0.12% and 0.16% in the Dynamit, Fiocchi and CCI primer, respectively.

The investigators in this study recommended that further testing be conducted to more precisely characterize these primers and assess their suitability for use in military ammunition (Ref 4).

An industrial hygiene survey was conducted at the State of Wisconsin, Department of Transportation State Police Headquarters Indoor Firing Range in 1994 (Ref 2). The purpose of the survey was to measure exposures to lead, tungsten, copper and total particulate while using Delta Defense frangible ammunition during a normal round of

qualification shooting using standard issue ammunition. The ammunition was produced by Delta Defense, and according to its material safety data sheet, the bullet is comprised of tungsten, copper and nylon 6. The propellant was a double base smokeless powder composed of nitrocellulose, nitroglycerin and stabilizers. A leadless primer was used. Two different manufacturers of primers were available for use with ammunition. Both were leadless, however, the Fiocchi had small amounts of antimony and bismuth, whereas the Winchester primer contained no such metals. The Fiocchi primer components were Diazodinitrophenol (DDNP), tetracene, barium nitrate and antimony sulfide. Due to the small amount of antimony and bismuth in the Fiocchi primer, the exposure would not be expected to cause adverse health effects. Sampling was done for lead, tungsten, copper and total particulates during the test period.

All shooters using the frangible ammunition had measurable exposures to lead, tungsten and copper. All of the exposures were below their respective eight-hour OSHA time-weighted average exposure limits. Since the ammunition contained no lead, the lead must have been present in the room from past activities. The shooters using standard ammunition had lead time-weighted average exposures below the OSHA 50 $\mu\text{g}/\text{m}^3$ PEL, however, the lead exposure during shooting were considerably higher than the shooters using the frangible ammunition. The range officer present during both types of ammunition shoots had an exposure to lead, tungsten and copper; however, the time-weighted averages were well below the OSHA action levels and PELs.

As a result of the study, the following recommendations were made.

- Thoroughly decontaminate the firing range and adjoining hallway of residual lead.
- Only non-lead ammunition such as Delta Defense frangible ammunition should be used in the shooting ranges, unless significant improvements in the ventilation system are made and shown to be effective.
- If shooting is to occur frequently, even with the use of non-lead ammunition, the ventilation needs to be improved to prevent contamination of the rest of the building with copper fume.
- If Delta Defense ammunition is to be used, specify the Winchester primer that contains no lead, antimony or barium.
- Perform wipe tests of the inside of HVAC ductwork, grilles, and other flat surfaces in the building to find if lead contamination is present. There are no guidelines as to the amount of lead to allow on a surface of ductwork. However, Maryland and Massachusetts recommend <200 micrograms per square foot on floors; therefore, levels of lead in ductwork should be kept below 50 micrograms per square foot, assuming airborne lead levels stay below the OSHA action level of 30 micrograms per cubic meter.

A 1994 DoE study evaluated the 9mm and 5.56-mm calibers of Delta frangible ammunition (DFA) for use as duty ammunition (Ref 3). Airborne sampling analyses were performed to determine if airborne particulates formed as a by-product to weapons firing pose unacceptable exposure levels to range users.

During the shooting tests, breathing zone sampling and area monitoring was performed to determine personnel exposures received from the substitute components in the ammunition. The components for which sampling was performed were chosen based on information contained in the MSDSs provided by each manufacturer. These components were copper fume, nitroglycerine, nitrogen dioxide, nitric oxide, carbon monoxide and tungsten. Data was compared to the most conservative limits established by either OSHA/NIOSH (PELs) or ACGIH (TLVs). Each constituent was sampled and analyzed by approved NIOSH procedures. Copper is one of the primary constituents of the Delta frangible ammunition. Copper is mostly contained in the jacket of the bullet and, once heated through the combustion process, it becomes a fume and then airborne. Tungsten is also one of the primary constituents and may become airborne during the combustion process.

The eight-hour exposure data were collected from two types of firing ranges, a twenty point outdoor range at the Rocky Flats Plant in Colorado, and a six lane indoor range at the Central Training Facility in Oak Ridge, Tennessee.

The Rocky Flats data showed no copper concentrations greater than 0.0039 mg/m^3 (TLV = 0.1 mg/m^3) at any firing lane; no tungsten concentration greater than 0.0017 mg/m^3 (TLV = 5.0 mg/m^3); no nitroglycerin concentration greater than 0.032 mg/m^3 (TLV = 0.1 mg/m^3); no nitrogen dioxide/nitric oxide concentration greater than 0.1 mg/m^3 . TLVs for nitrogen dioxide and nitric oxide are 1.8 mg/m^3 and 30 mg/m^3 , respectively. Carbon monoxide was not detected using Drager tubes. Concentrations at the instructor positions were generally lower than these reported values.

Similar data at the Oak Ridge indoor range showed no copper concentrations greater than 0.055 mg/m^3 , no tungsten concentrations greater than 0.04 mg/m^3 , no nitroglycerin concentrations greater than 0.03 mg/m^3 , and no carbon monoxide concentrations greater than 7.3 mg/m^3 . Concentrations at the instructor positions were generally lower than these reported values.

The overall findings supported substitution of the tested components for the standard lead ammunition. Advantages of making the substitution include:

- Results of the breathing zone and area monitoring tests revealed that the substitute components in the ammunition did not exceed established limits and do not pose unacceptable health risk to personnel. The ammunition types present an unlikely health risk when used under the correct exposure conditions.
- The tested components will provide a safer environment for employees exposed to harmful airborne particulates at DoE ranges.
- The tested components will eliminate the mandatory semi-annual blood lead testing programs and significantly reduce the required airborne monitoring requirements.

The Department of the Army, in a TECOM Safety Release (Ref. 18), supported the use of lead-free ammunition from a health and safety perspective. With respect to toxic fumes, it concluded that the 5.56mm and 9mm frangible ammunition produce equivalent levels of carbon monoxide, ammonia, and nitrous oxide gases when compared to the standard

ball ammunition types. The lead levels recorded were below the levels produced by the M855 (5.56mm) and M882 (9mm) ball cartridges. The lead levels recorded with the test ammunition should be considered as residue from the ball cartridges left inside the sealed test chamber.

4.2.2.2 Noise Exposure. There have been a limited number of studies done comparing the noise levels from lead-free ammunition with those from conventional ammunition. The Department of the Army, in a TECOM Safety Release (Ref. 18), concluded that the results of tests indicated that the ammunition produces equivalent impulse noise levels as the standard ammunition. The 140dB contour is set at 30 meters and single hearing protection is required.

Substantiating this conclusion was a study done by the U.S. Army Aberdeen Test Center (Ref 1). The objective of this test was to determine the impulse noise levels produced by the 5.56 and 9-mm frangible training ammunition when fired from various service weapons. Testing was conducted for two conditions. The first scenario was in an area free of any sound-reflecting surfaces within 15 meters of the weapon. In the second scenario, the test firings were conducted inside an enclosed range.

For test firings conducted in the open, peak sound pressure levels and A- and B- pulse durations were determined for each round fired. These data are shown in Table 8. Three microphones, B&K model No 4136 were placed approximately 1.5 meters above the ground, 5 meters from the shooter, and at angles 180° (e.g., south of shooter), 225° and 270°. In addition, recordings were made at the shooter's left ear (weapon fired right-handed).

Table 8. Impulse Noise Levels, Open Air Range.

	Ammunition		Microphone Location	Peak Impulse Noise Levels		
Weapon	Caliber	Type		Duration, ms		Noise Level, dB
				A	B	
M9	9-mm	Frangible	Shooter	0.33	3.0	156.2
			270°	0.40	3.7	148.2
			225°	0.39	4.0	142.7
			180°	0.39	5.3	137.5
		M882 Ball	Shooter	0.24	3.3	157.2
			270°	0.31	4.5	148.4
			225°	0.28	4.1	142.8
			180°	0.41	4.4	139.5
M16A1	5.56-mm	Frangible	Shooter	0.39	4.8	158.6
			270°	0.46	5.0	152.5
			225°	0.40	5.4	146.5
			180°	0.77	8.0	140.8
		M855 Ball	Shooter	0.44	5.4	158.9
			270°	0.48	5.0	152.0
			225°	0.37	5.3	146.3
			180°	0.65	7.1	139.4
GUU5P	5.56-mm	Frangible	Shooter	0.32	4.2	161.7
			270°	0.42	4.4	152.4
			225°	0.30	4.4	147.6
			180°	0.73	7.3	140.8
		M855 Ball	Shooter	0.26	4.8	161.7
			270°	0.51	3.8	161.7
			225°	0.41	4.9	147.3
			180°	0.61	5.6	141.7

For firings in the enclosed range, all levels were recorded for the shooter's ear position only. These data are shown in Table 9.

Table 9. Impulse Noise Levels, Enclosed Range.

	Ammunition		Microphone Location	Peak Impulse Noise Levels		
Weapon	Caliber	Type		Duration, ms		Noise Level, dB
				A	B	
M9	9-mm	Frangible	Shooter	0.25	200.0	156.3
		M882 Ball		0.33	140.1	155.3
M16A1	5.56-mm	Frangible		0.44	166.5	159.2
		M855 Ball		0.46	200.0	161.1
GUU5P	5.56-mm	Frangible		0.28	113.7	162.0
		M855 Ball		0.30	137.7	161.7

Technical analysis of the data indicated that the shooter required single hearing protection when firing the 5.56- and 9-mm frangible ammunition. Based on the 140-dB contour distances, single hearing protection was required within 30 meters for the 5.56-mm frangible ammunition and within 20 meters for the 9-mm frangible ammunition. The number of daily exposures was greater than 200 rounds for each type of ammunition. There was not a significant difference between the frangible and conventional (e.g., M855 Ball) ammunition.

Noise monitoring was also done as part of a DoE study (Ref 3) to establish baseline measurements during the use of the Delta frangible ammunition. Measurements taken at the Rocky Flats outdoor firing range are shown in Table 10. Two types of monitoring equipment were used at Rocky Flats: the Metrosonic db-3100 Sound Analyzer; and the Quest M-27 Noise Logging Dosimeter. The obtained eight-hour time weighted averages varied from a low of 86.0 dB to 90.4 dB over the 20 firing lane positions. Results were compared to historical firing range noise data shown in Table 11. The authors concluded that the "non-toxic" ammunition demonstrated noise levels slightly higher than the regular ammunition but that additional testing would be necessary to actually make a valid comparison. It should be noted, however, that the historic data did not provide lane positions so a point by point comparison was not made. Also, test details for the historic data were not provided so other contributing factors may not be properly described.

Table 10. Noise Results from Rocky Flats Outdoor Firing Range (Non-Toxic Ammo)

Lane Position	Noise Level (non-toxic) TWA
1	voided
2	86
3	79.4*
4	87.7*
5	85.1*
6	not monitored
7	86.0*
8	not monitored
9	not monitored
10	not monitored
11	87.5*
12	not monitored
13	not monitored
14	not monitored
15	90.4*
16	not monitored
17	90.4*
18	87.3
19	89.6*
20	not monitored

*Quest M-27 Noise Logging Dosimeter

Table 11. Historic Noise Results from Rocky Flats Outdoor Range (Regular Ammo)

Noise Level (regular ammo) TWA (db)
77.0
74.9
76.8
76.8
80.0
80.0
84.1

Similar data acquired at the Oak Ridge indoor range, using the Metrosonic db-3100 instrument, is shown in Table 12. The eight-hour time weighted averages varied from a low of 87.3 dB to a high of 104.2 dB over the nine positions (six firing lanes and three instructor positions). The investigators reported that the noise data were comparable with standard ammunition data (Ref 3).

Table 12. Noise Results from Oak Ridge Indoor Firing Range (Non-Toxic Ammo)

Lane Position	8-hr time weighted average in decibels (db)
1	102.2
2	103.0
3	104.2
4	103.1
5	103.5
6	101.0
7*	87.3
8*	98.8
9*	101.2

*Instructors behind line

4.3 Risk Characterization

In the risk characterization step, the risk assessor determines the most critical site risks and whether they are great enough to cause health problems for people at or near a site. The results of the three previous steps (e.g., data analysis, hazard identification, exposure analysis) are combined, evaluated, and summarized. Risk assessors add up potential risks from the individual chemicals and pathways and calculate a total site risk. They also

consider the amount of uncertainty in the risk estimates. Risk assessment results are then factored into decisions on how best to clean up the site during the risk management phase.

Because the lead-free ammunition alternatives have not yet been used extensively, the real value of thinking through the risk exposure and risk characterization steps of the risk assessment process is to control future risks to an acceptable level. That is, the risk assessment framework currently used for evaluating contaminated sites provides a basis for asking the right questions and making risk-based decisions ahead of time and, hopefully, head off downstream remediation.

5.0 Conclusions

The major conclusions from this review are:

- Because of the known high toxicity of lead, relative to what is known about the toxicity of lead-free alternatives, the alternatives are preferred from a human health and environmental quality viewpoint. This is true for both projectiles and primers.
- Though preferable to lead, significant data gaps exist on the toxicology of lead-free ammunition components.
- Being lead-free does not necessarily make small arms ammunition toxic-free.
- Some ammunition available on the market has lead-free projectiles but still utilizes lead compounds in the primer. This ammunition reduces environmental (downrange) concerns. However, its use does not eliminate the potential exposure to lead at the firing line positions. This is especially true at indoor ranges where ventilation systems must control the dust concentration (containing lead and lead compounds mainly from the primer) to an acceptable level.
- Ammunition manufacturers will typically provide very limited information on the composition of primer and propellant composition because of the proprietary nature. Some MSDSs have a reasonable amount of information but many do not.
- Though the use of lead-free or reduced lead ammunition has been a subject of study and testing for many years, human health effects and environmental quality effects have not been well studied and documented.
- There is not a significant difference in the noise exposure for the lead-free ammunition as compared to traditional ammunition.

6.0 Recommendations

Based on the conclusions, it is recommended that:

- Use a risk management approach to substitute lead free ammunition for conventional ammunition for training purposes.
 - Identify possible health-related issues associated with alloy metal when used alone and when present in combination with tungsten and other alloy metals. This will identify synergistic effects, if any, resulting from exposure to more than one metal.
 - Conduct baseline industrial hygiene and environmental surveys at selected firing ranges using the replacement ammunition. The surveys should include air

sampling for lead (residual from prior use), tungsten and copper for the Winchester ammunition. Also, the decomposition products of carbon monoxide, ammonia and nitrogen dioxide should be monitored. In general, since a variety of ammunition may be used, sampling requirements should be determined on a case-by-case basis from the manufacturer's MSDSs. Swipe sampling for residual lead, ventilation system evaluation, and noise monitoring should be accomplished at indoor ranges. Environmental considerations should include dust control in the bullet trap area and other contaminant pathway factors such as storm water control and extent of lead contamination from prior use of leaded ammunition.

- Until there is replacement ammunition that is adopted by the military, carefully confirm the composition of all lots of replacement ammunition since manufacturers seem to be changing the composition in search of the "optimal."
- Train instructors and shooters that being lead-free does not remove all concern for exposure to hazardous materials.
- Establish effective communications with other organizations interested in the use of lead-free ammunition.
- Create a database to consolidate knowledge on lead-free ammunition, as it becomes available through literature search, communications with industry and information exchange with government organizations (e.g., DoD, FBI, DoE, etc.).
 - Capture operational lessons learned with respect to human health and environmental implications.
 - Track the manufacturing trends and formulation changes in ammunition with regard to human health and environmental implications.
 - Conduct an extensive literature search on the toxicology of chemicals used in lead-free ammunition. Keep abreast of latest developments in the toxicology of lead-free ammunition components through technical literature and personal contacts with other using organizations.

7.0 REFERENCES

Organization Points of Contact

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Useful Web Sites

- Army Green Ammunition Program Office
www.w3.pica.army.mil/greenammo/projects.htm
- ChemFinder Web Server <http://www.chemfinder.com/siteslist.html>
- Risk Assessment Information System http://risk.lsd.ornl.gov/rap_hp.htm
- EPA Integrated Risk Information System
<http://www.epa.gov/ngispgm3/iris/index.html>
- Internet Resources for MSDS <http://www.ilpi.com/msds/index.html#General>
- OSHA Technical Manual, Chapter 5 on Noise. <http://www.osha-slc.gov/dts/osta/otm/otmiii/otmiii5.html>

- Superfund Risk Assessment <http://www.epa.gov/superfund/programs/risk/>
- Vermont MSDS <http://hazard.com/msds/index.html>
- MSDS (Cornell) <http://msds.pdc.cornell.edu/ISSEARCH/MSDSsrch.HTM>
- Environmental Professionals Homepage <http://www.clay.net/ep.html>
- MSDS (Oxford) <http://physchem.ox.ac.uk/MSDS/>
- National Center for Environmental Assessment <http://www.epa.gov/ncea/>
- Joint Service Pollution Prevention Library <http://enviro.nfesc.navy.mil/p2library/>
- Defense Environmental Network and Information Exchange (DENIX)
<http://www.denix.osd.mil/>

Appendix A

Toxicity of Lead-Free Ammunition to Wildlife

Toxicity Information of Selected Lead-Free shot on game birds and mammals as summarized from the Federal Register (19 Aug 1999). References have been removed from this appendix. They can be found on the Fish and Wildlife Service web site.

There is considerable difference in the toxicity of soluble and insoluble compounds of tungsten and iron. Elemental tungsten and iron are virtually insoluble and are therefore expected to be relatively nontoxic. Even though most toxicity tests reviewed were based on soluble tungsten compounds rather than elemental tungsten, there appears to be no basis for concern of toxicity to wildlife for either candidate shot via ingestion by fish or mammals (Bursian et al. 1996b, Gigiena 1983, Karantassis 1924, Patty 1982, Industrial Medicine 1946). Detailed reviews of the toxicological impacts of different tin compounds have been conducted by Eisler (1989) and Cooney (1988). Both reviews indicate that elemental tin is non-toxic to animals. Tin shot designed for waterfowl hunting is utilized in several European countries and no reports exist that suggest that tin shot is causing toxicity problems for wildlife in those countries. The potential toxicity of nylon compounds due to degradation is primarily associated with the stabilizers, antioxidants, plasticizers, and unreacted prepolymers. Residual caprolactum has been found in some commercial Nylon 6 products, but little concern regarding this compound has been developed (Patty, 1982). The toxicity of Nylon 6 and 11 are negligible due to their insolubilities.

Environmental Fate and Transport

Tungsten is insoluble in water and therefore not mobile in hypergenic environments. Tungsten is very stable with acids and does not easily complex. Preferential uptake by plants in acid soil suggests uptake of tungsten in the anionic form associated with tungsten minerals rather than elemental tungsten (Kabata and Pendias 1984). Tin pellets will undergo slow surface oxidation to form hydrated tin oxide, which is extremely insoluble in water (Lide 1990). Therefore dissolution will be slow, and highly localized aqueous concentrations will not arise. This means that elemental tin will over time remain largely in the same inorganic form as when it is discharged. Tin pellets discharged into wetlands where sulphur ions are released during organic decomposition would become coated with tin sulphide, which is highly insoluble in water and resistant to aquatic hydrolysis (Hoiland 1995).

Environmental Concentration

The estimated environmental concentration (EEC) for a terrestrial ecosystem was calculated based on 69,000 shot per hectare (Pain 1990), assuming complete erosion of

material in 5 cm of soil. For tungsten-iron shot, the EEC for tungsten in soil was calculated at 32.9 mg/kg. For tungsten-polymer shot, the EECs for tungsten and Nylon (6 and 11) in soil are 58.3 mg/kg and 2.7 mg/kg, respectively. The EECs for tungsten and the 2 polymers found in tungsten-matrix are 25.7 mg/kg, 4.2 mg/kg, and 0.14 mg/kg, respectively. The EEC for tin in soil is 19.3 g/m^3 .

The effective environmental concentration (EEC) for an aquatic ecosystem was calculated assuming complete erosion of the shot in one cubic foot of water. For tungsten-iron shot, the EEC in water for tungsten was 10.5 mg/L. For tungsten-polymer shot, the EECs in water for tungsten and Nylon (6 and 11) are 18.7 mg/L and 0.9 mg/L, respectively. The EECs in water for tungsten and the 2 polymers found in tungsten-matrix are 4.2 mg/L, 0.2 mg/L, and 0.02 mg/L, respectively. The EEC in water for tin is 19.3 mg/L.

Effects on Birds

An extensive literature review in each application provided information on the toxicity of elemental tungsten and tin to waterfowl and other birds. Ringelman et al. (1993) orally dosed 20 8-week-old game-farm mallards with 12-17 (1.03 g average weight) tungsten-bismuth-tin (TBT) pellets and monitored them for 32 days for evidence of intoxication. No birds died during the trial, gross lesions were not observed during the postmortem examinations, histopathological examinations did not reveal any evidence of toxicity or tissue damage, and tungsten was not detectable in kidney or liver samples. The authors concluded that TBT shot presented virtually no potential for acute intoxication in mallards.

Kraabel et al. (1996) assessed the effects of embedded TBT shot on mallards and concluded that TBT was not acutely toxic when implanted in muscle tissue. Inflammatory reactions to TBT shot were localized and had no detectable systemic effects on mallard health.

Nell (1981) fed laying hens (*Gallus domesticus*) 0.4 or 1.0 g/kg tungsten in a commercial mash for five months to assess reproductive performance. Weekly egg production was normal and hatchability of fertile eggs was not affected. Exposure of chickens to large doses of tungsten either through injection or by feeding resulted in an increased tissue concentration of tungsten and a decreased concentration of molybdenum (Nell 1981). The loss of tungsten from the liver occurred in an exponential manner with a half-life of 27 hours. The alterations in molybdenum metabolism seemed to be associated with tungsten intake rather than molybdenum deficiency. Death due to tungsten occurred when tissue concentrations increased to 25 mg/g liver. At that concentration, xanthine dehydrogenase activity was zero.

Ringelman et al. (1992) conducted a 32-day acute toxicity study, which involved dosing game-farm mallards with a shot alloy of tungsten-bismuth-tin (TBT), which was 39, 44.5 and 16.5 percent by weight, respectively. No dosed birds died during the trial, and behavior was normal. Examination of tissues post-euthanization revealed no toxicity

or damage related to shot exposure. This study concluded that "... TBT shot presents virtually no potential for acute intoxication in mallards under the conditions of this study."

Several studies have been conducted in which pellets made of tin or tin alloys have been placed inside the digestive tract or tissues of ducks to determine if toxic effects occur. Grandy et al. (1968) and the Huntingdon Research Centre (1987) conducted 30- and 28-day, respectively, acute toxicity tests on mallard ducks and reported that all treatment ducks survived with insignificant weight loss or development of pathological lesions. The potential for bismuth-tin (BT) shot to produce toxicological effects in ducks during reproduction has been investigated under both acute and chronic testing conditions. Tin as a 2% component of the tested shot, did not pose a toxic risk to ducks when fed a nutritionally-imbalanced, corn-based diet. Neither has BT shot been shown to pose an adverse risk to the health of ducks, the reproduction by male and female birds, nor the survival of ducklings over the long term (Sanderson et al. 1997a,b).

Nylon 6 is the commercially important homopolymer of caprolactum. Most completely polymerized nylon materials are physiologically inert, regardless of the toxicity of the monomer from which they are made (Peterson 1977). Few data exist on the toxicity of Nylon 6 in animals. Most toxicity studies are related to thermal degradation products and so are not relevant to the exposure of wildlife to shot containing nylon. Montgomery (1982) reported that feeding Nylon 6 to rats at a level of 25 percent of the diet for 2 weeks caused a slower rate of weight gain, presumably due to a decrease in food consumption and feed efficiency. However, the rats suffered no anatomic injuries due to the consumption of nylon.

The two plastic polymers used in tungsten-matrix shot act as a physical matrix in which the tungsten is distributed as ionically-bound fine particles. Most completely polymerized nylon materials are physiologically inert, regardless of the toxicity of the monomer from which they are made (Peterson 1977). A literature review did not reveal studies in which either of the two polymers were evaluated for toxicity in birds.

Acute Toxicity Studies

Federal contracted with Michigan State University—Department of Animal Science, to conduct an acute toxicity study of tungsten-iron and tungsten-polymer. Both Kent and ITRI contracted with Wildlife International Ltd. To conduct an acute toxicity study of tungsten- matrix and tin shots, respectively. The acute toxicity test is a short- term (30-day) study where ducks are dosed with shot and fed commercially available duck food. Survival, body weight, blood hematocrit, and organ analysis are recorded.

Tungsten-iron and tungsten-polymer

The 30-day dosing study revealed no adverse effects when mallards were dosed with either 8 BB size tungsten-iron shot or 8 BB size tungsten-polymer shot and monitored

over a 30-day period (Bursian et al. 1996a, Bursian et al. 1996b). Eight male and 8 female adult mallards were dosed with either 8 No.4 steel shot, 8 No.4 lead shot, 8 BB size tungsten-iron shot, or 8 BB size tungsten-polymer shot and observed over a 30-day period. An additional 8 males and 8 females received no shot. Fifty percent of the lead-dosed birds (5 males and 3 females) died during the 30-day test while there were no mortalities in the other groups. Lead-dosed birds were the only ones to display green excreta, lethargy, and ataxia. Body weights were not significantly altered by any of the treatments, although lead-dosed birds, which died during the trial, lost an average of 30 percent of their body weight. Hematocrit, hemoglobin concentrations, and ALAD activity were significantly depressed at day 15 in the lead-dosed females, while lead-dosed males had significantly depressed hematocrit and hemoglobin concentration compared with the other four groups. There were no significant differences in these whole-blood parameters at day 30. Three tungsten-polymer-dosed males developed mild biliary stasis. The authors attributed this to the intubating of mallards with 8 BBs of tungsten-polymer shot inducing a pathological condition—however slight—that was not found in the control birds. No other histopathological lesions were found. Tungsten was detected in the femur of two tungsten-polymer-dosed females and the kidneys of two tungsten-polymer-dosed birds; in both tissues, concentrations were only slightly above detection limits. In general, no adverse effects were seen in mallards given 8 BB-size tungsten-polymer shot and monitored over a 30-day period.

Tungsten-matrix

Kent's 30-day dosing study (Wildlife International Ltd. 1998a) included 4 treatment and 1 control group of game-farm mallards. Treatment groups were exposed to 1 of 3 different types of shot: 8 #4 steel, 8 #4 lead, or 8 #4 tungsten-matrix; whereas the control group received no shot. The 2 tungsten-matrix treatment groups (1 group deficient diet, 1 group balanced diet) each consisted of 16 birds (8 males and 8 females); whereas remaining treatment and control groups consisted of 6 birds each (3 males and 3 females). All tungsten-matrix-dosed birds survived the test and showed no overt signs of toxicity or treatment-related effects on body weight. There were no differences in hematocrit or hemoglobin concentration between the tungsten-matrix treatment group and either the steel shot or control groups. No histopathological lesions were found during gross necropsy. In general, no adverse effects were seen in mallards given 8 #4 size tungsten-matrix shot and monitored over a 30-day period. Tungsten was found to be below the limit of detection in all samples of femur, gonad, liver, and kidney from treatment groups.

Tin

ITRI's 30-day dosing study (Wildlife International Ltd. 1998b) included 4 treatment and 1 control group of game-farm mallards. Treatment groups were exposed to 1 of 3 different types of shot: 8 #4 steel, 8 #4 lead, or 8 #4 tin shot; whereas the control group received no shot. The 2 tin treatment groups (1 group deficient diet, 1 group balanced diet) each consisted of 16 birds (8 males and 8 females); whereas remaining treatment and control groups consisted of 6 birds each (3 males and 3 females). All tin-dosed birds

survived the test and showed no overt signs of toxicity or treatment-related effects on body weight. There were no differences in hematocrit or hemoglobin concentration between the tin treatment group and either the steel shot or control groups. No histopathological lesions were found during gross necropsy. In general, no adverse effects were seen in mallards given 8 #4 size tin shot and monitored over a 30-day period. No levels of tin above the limit of detection were observed in any tissues collected from either tin treatment group.

Reproductive/Chronic Toxicity Study

Federal contracted with Michigan State University—Department of Animal Science, to conduct an a reproductive/chronic toxicity studies for both tungsten-iron and tungsten-polymer shot types. The reproductive/chronic toxicity study is a long-term (150-day) study where ducks are dosed with shot and fed commercially available duck food. Survival, body weight, blood hematocrit, organ analysis, and reproductive performance are recorded.

Tungsten-Iron and Tungsten-Polymer

The reproductive/chronic toxicity study revealed no adverse effects when mallards were dosed with either 8 No. 4 size tungsten-iron shot, or 8 No. 4 size tungsten-polymer shot, and monitored over a 150-day period (Bursian et al. 1999). Sixteen male and 16 female adult mallards were orally dosed with either 8 No.4 steel shot, 8 No.4 tungsten-iron shot, or 8 No. 4 tungsten-polymer shot. An additional 6 male and 6 female mallards were dosed with 8 No. 4 lead shot. All lead-dosed birds died by day 25 of the study, whereas no mortalities occurred in the other test groups. Lead-dosed birds had significantly decreased hematocrit, hemoglobin concentration and whole-blood delta aminolevulinic dehydratase activity on day 7 of the study. Mallards dosed with tungsten-iron or tungsten-polymer shot had occasional significant differences in hematocrit and plasma chemistry values when compared to steel-dosed mallards over the 150-day period, but these changes were within the normal range reported for mallards and were not considered to be deleterious. Relative kidney, heart, brain and gizzard weights of lead-dosed birds were significantly greater in comparison to relative weights of those organs in the other 3 treatment groups. Marked liver hemosiderosis was present in all steel and tungsten-dosed males, in 5 of 8 steel-and 3 of 8 tungsten-iron-dosed females, and in 1 tungsten-polymer-dosed male examined. Small amounts of tungsten were detected in gonad and kidney samples from males and females, in femur samples of males, and in liver samples from females dosed with tungsten-polymer shot. Higher concentrations of tungsten were detected in femur, gonad, kidney, and liver samples from tungsten-iron-dosed ducks. The rate of shot erosion was 99% for tungsten-polymer, 72% for tungsten-iron, 55% for steel, and 37% for lead. There were no significant differences in percent egg production, and percent fertility and hatchability of eggs from tungsten-iron- and tungsten- polymer-dosed ducks when compared to steel-dosed ducks. There were no biological differences in percent survivability and body weight of ducklings from tungsten-iron-or tungsten-polymer-dosed ducks when compared to ducklings from steel-

dosed ducks. The hematocrit of ducklings from tungsten-iron-dosed ducks was slightly but significantly lower when compared to ducklings from steel-dosed ducks. Histological examination of duckling kidneys and liver indicated no abnormalities. Tungsten was detected in 25%, 9%, and 13% of the femur, kidneys, and liver samples, respectively, from ducklings of the tungsten-iron and tungsten-polymer groups. Overall, results of this study indicated that tungsten-iron and tungsten-polymer shot repeatedly administered to adult mallards did not adversely affect them or the offspring they produced during the 150-day trial.

Nontoxic Shot Approval

The first condition of nontoxic shot approval is toxicity testing. Based on the results of the toxicological report and the toxicity tests Tiers 1, 2, and 3) discussed above, we conclude that tungsten-iron and tungsten-polymer shot does not pose a significant danger to migratory birds or other wildlife and their habitats. Based on the results of toxicological reports and acute toxicity tests (Tier 1 and 2), we conclude that tungsten-matrix and tin shots do not appear to pose a significant danger to migratory birds and other wildlife and their habitats.

In a similar manner, the toxicity of bismuth-tin was reviewed in the Federal Register/Vol. 62, No.21/January 31, 1997. As a result of the required toxicity tests (acute, chronic and reproductive effects), the Fish and Wildlife Service concluded that bismuth-tin shot composed of 97 parts bismuth and 3 parts tin with <1 percent residual lead does not impose a significant danger to migratory birds and other wildlife and their habitats (Ref 11).

APPENDIX B

TUNGSTEN AND COMPOUNDS (insoluble)

FROM: EPA IRIS

CAS: 7440-33-7; Chemical Formula: W

The references have been removed from the appendix. They can be found on the EPA IRIS web site.

Previously, OSHA had no exposure limits for insoluble tungsten and its compounds. The ACGIH has established 5 mg/m³ as an 8-hour TWA and 10 mg/m³ as a short-term exposure limit for these substances. NIOSH recommends a limit of 5 mg/m³ as a 10-hour TWA. The proposed PEL for this group of substances was 5 mg/m³ as an 8-hour TWA and 10 mg/m³ as a 15-minute STEL. NIOSH (Ex. 8-47) concurred with OSHA's proposed limits. The final rule promulgates a 5 mg/m³ 8-hour TWA and a 10 mg/m³ 5-minute STEL, measured as tungsten. Tungsten is a gray, hard metal. Rats fed a diet containing 0.5 percent insoluble tungsten compounds died, and another group of rats fed 0.1 percent of these compounds suffered noticeable weight loss (Kinard and Van de Erve 1941/Ex. 1-492). Studies in rats fed tungsten at 2, 5, or 10 percent of their diet showed that females in all dose groups had a 15-percent reduction in weight gain (Kinard and Van de Erve 1943/Ex. 1-493). The intraperitoneal LD (50) for tungsten metal powder in rats was 5 g/kg body weight; survivors showed minor liver and spleen changes at necropsy (Fredrick and Bradley 1946, as cited in ACGIH 1986/Ex. 1-3, p. 614). Studies of the tissues of guinea pigs intratracheally injected with tungsten metal and tungsten carbide revealed moderate interstitial cellular proliferation and no changes, respectively. However, Soviet studies involving similar intratracheal injections showed proliferation of the intra-alveolar septa (Kaplun and Mezentseva 1960, as cited in ACGIH 1986/Ex. 1-3, p. 614). The NIOSH criteria document for tungsten (1977h, as cited in ACGIH 1986/Ex. 1-3, p. 614) reports that Russian investigators found a 9- to 11-percent incidence of pulmonary fibrosis in workers exposed to tungsten (Kaplun and Mezentseva 1959/Ex. 1-961; and Mezentseva 1967, as cited in ACGIH 1986/Ex. 1-3, p. 614). NIOSH (1977h) recommended that the standard for tungsten and its insoluble compounds be set at 5 mg/m³ to protect against pulmonary effects.

Stokinger (in Patty's Industrial Hygiene and Toxicology, 3rd rev. ed., Vol. 2A, Clayton and Clayton 1981) reported on several epidemiological studies of workers in the "hard metal industry," in which tungsten carbide is machined. These studies describe a condition known as hard metal disease, which may be accompanied by pulmonary fibrosis. The disease is characterized by a moderate incidence of cough, dyspnea, and wheezing, a high incidence of minor radiological abnormalities with a few instances of marked abnormalities, and development of hypersensitivity asthma in some workers (which may be due to exposure to the cobalt that is used as a binding agent). The disease is progressive and potentially lethal. Stokinger (in Patty's Industrial Hygiene and Toxicology, 3rd rev. ed., Vol. 2A, Clayton and Clayton 1981, p. 1992) reported that, unlike other lung diseases produced by inorganic dust, there is no correlation between onset of symptoms, length of exposure, and the development of interstitial fibrosis. Analysis of the lung of one worker who had clinical signs and radiological changes

showed the presence of large amounts of tungsten with much smaller amounts of other metals.

Mr. H.K. Thompson, Corporate Industrial Hygiene Manager for Caterpillar, Inc. (Ex. 3-349), questioned the need for a STEL for tungsten. OSHA believes that, given the potential seriousness of hard metal disease and the uncertainties regarding the relationship between exposure and response, a short-term limit for tungsten will provide additional assurance that the 8-hour TWA PEL is not exceeded. Therefore, in accordance with OSHA's policy for establishing STELs in this rulemaking (see Section IV.C.17), OSHA finds that a STEL for tungsten is necessary.

In the final rule, OSHA is establishing an 8-hour TWA of 5 mg/m³ and a STEL of 10 mg/m³ for tungsten and its insoluble compounds, measured as tungsten. The Agency concludes that these limits will substantially reduce the significant risk of pulmonary fibrosis and other lung effects, which constitute material impairments of health that are associated with exposure to this metal and its insoluble compounds at levels above the new PELs.

APPENDIX C

TUNGSTEN AND COMPOUNDS (soluble)

FROM: EPA IRIS

CAS: 7440-33-7; Chemical Formula: W

The references have been removed from the appendix. They can be found on the EPA IRIS web site.

OSHA had no former limit for exposure to tungsten and its soluble compounds. The ACGIH limit is 1 mg/m³ TWA, with a 3 mg/m³ STEL, measured as tungsten. NIOSH recommends a 1 mg/m³ 10-hour TWA for tungsten and its soluble compounds. OSHA proposed an 8-hour TWA PEL of 1 mg/m³ and a 15-minute STEL of 3 mg/m³; NIOSH (Ex. 8-47, Table N1) concurred with the addition of a STEL to the 1 mg/m³ TWA limit. The final rule establishes limits of 1 mg/m³ as an 8-hour TWA and 3 mg/m³ as a 15-minute STEL, measured as tungsten. Tungsten is a grey, hard metal.

Animal studies have shown that the LD(50) for soluble sodium tungstate when injected subcutaneously in rats ranges from 140 to 160 mg/kg (Kinard and Van de Erve 1940/Ex. 1-788). Soluble tungsten's lethal effects are the result of systemic poisoning that occurs as the compound is absorbed by multiple organs; this is followed by cellular asphyxiation (International Labour Office [ILO] 1934c, as cited in ACGIH 1986/Ex. 1-3, p. 614). Karantassis (1924, as cited in ACGIH 1986/Ex. 1-3, p. 614) also observed a systemic response in guinea pigs given soluble sodium tungstate or pure soluble tungsten either orally or intravenously; the animals developed anorexia, colic, trembling, and difficulty in breathing prior to death. Rats fed a diet containing 0.5 percent tungsten as soluble sodium tungstate or tungsten oxide died from this dose. Dietary doses of 0.1 percent tungsten oxide and the sodium salt caused weight loss in rats, but no deaths (Kinard and Van de Erve 1941/Ex. 1-492). Tungsten is believed to act by antagonizing the action of molybdenum (Higgins, Richert, and Westerfield 1956/Ex. 1-487). In its criteria document for tungsten (1977h, as cited in ACGIH 1986/Ex. 1-3, p. 614), NIOSH states that information on the effects of exposure to soluble tungsten compounds in the working population is not available. The ACGIH (1986/Ex. 1-3, p. 614) recommends a lower TLV for the soluble, as compared to the insoluble, compounds of tungsten because of the former's greater systemic toxicity. No comments other than those of NIOSH (Ex. 8-47) were received on this substance. In the final rule, OSHA is establishing an 8-hour TWA of 1 mg/m³ and a STEL of 3 mg/m³ for tungsten and its soluble compounds, measured as tungsten. The Agency concludes that these limits will protect workers against the significant risks of systemic toxicity, anorexia, colic, incoordination, trembling, and dyspnea, all of which constitute material health impairments that are associated with exposure to these compounds at levels above the new PELs.

APPENDIX D

Copper

CASRN 7440-50-8

The following information was extracted from the EPA IRIS database.

The references have been removed from the appendix. They can be found on the EPA IRIS web site.

I. CHRONIC HEALTH HAZARD ASSESSMENTS FOR NONCARCINOGENIC EFFECTS

I.A. REFERENCE DOSE FOR CHRONIC ORAL EXPOSURE (RfD)

Not available at this time.

I.B. REFERENCE CONCENTRATION FOR CHRONIC INHALATION EXPOSURE (RfC)

Not available at this time.

II. CARCINOGENICITY ASSESSMENT FOR LIFETIME EXPOSURE

Section II provides information on three aspects of the carcinogenic assessment for the substance in question; the weight-of-evidence judgment of the likelihood that the substance is a human carcinogen, and quantitative estimates of risk from oral exposure and from inhalation exposure. The quantitative risk estimates are presented in three ways. The slope factor is the result of application of a low-dose extrapolation procedure and is presented as the risk per (mg/kg)/day. The unit risk is the quantitative estimate in terms of either risk per ug/L drinking water or risk per ug/cum. air breathed. The third form in which risk is presented is a drinking water or air concentration providing cancer risks of 1 in 10,000, 1 in 100,000 or 1 in 1,000,000. The rationale and methods used to develop the carcinogenicity information in IRIS are described in The Risk Assessment Guidelines of 1986 (EPA/600/8-87/045) and in the IRIS Background Document. IRIS summaries developed since the publication of EPA's more recent Proposed Guidelines for Carcinogen Risk Assessment also utilize those Guidelines where indicated (Federal Register 61(79):17960-18011, April 23, 1996). Users are referred to Section I of this IRIS file for information on long-term toxic effects other than carcinogenicity.

II.A. EVIDENCE FOR CLASSIFICATION AS TO HUMAN CARCINOGENICITY

II.A.1. WEIGHT-OF-EVIDENCE CLASSIFICATION

Not classified. Basis -- There are no human data, inadequate animal data from assays of copper compounds, and equivocal mutagenicity data.

II.A.2. HUMAN CARCINOGENICITY DATA

None.

II.A.3. ANIMAL CARCINOGENICITY DATA

Inadequate. Bionetics Research Labs (1968) studied the carcinogenicity of a copper-containing compound, copper hydroxyquinoline, in two strains of mice (B6C3F1 and B6AKF1). Groups of 18 male and 18 female 7-day-old mice were administered 1000 mg copper hydroxyquinoline/kg bw (180.6 mg Cu/kg) suspended in 0.5% gelatin daily until they were 28 days old, after which they were administered 2800 ppm (505.6 ppm Cu) in

the feed for 50 additional weeks. No statistically significant increases in tumor incidence were observed in the treated 78-week-old animals.

In the same study, Bionetics Research Labs (1968) administered a single subcutaneous injection of gelatin (control) or 1000 mg of copper hydroxyquinoline/kg bw (180.6 mg Cu/kg) suspended in 0.5% gelatin to groups of 28-day-old mice of both strains. After 50 days of observation, the male B6C3F1 had an increased incidence of reticulum cell sarcomas compared with controls. No tumors were observed in the treated male B6AKF1 mice, and a low incidence of reticulum cell sarcomas was observed in the treated female mice of both strains.

Gilman (1962) administered intramuscular injections containing 20 mg of cupric oxide (16 mg Cu), cupric sulfide (13.3 mg Cu), and cuprous sulfide (16 mg Cu) into the left and right thighs of 2- to 3-month-old Wistar rats. After 20 months of observations, no injection-site tumors were observed in any animals, but other tumors were observed at very low incidence in the animals receiving cupric sulfide (2/30) and cuprous sulfide (1/30). As the relevance of the organic copper compound to the observation of sarcoma induction is uncertain and the incidence of tumors in rats treated i.m. with inorganic copper was very low, data are considered inadequate for classification.

II.A.4. SUPPORTING DATA FOR CARCINOGENICITY

Moriya et al. (1983) reported no increase in mutations in *E. coli* and *S. typhimurium* strains TA98, TA1535, TA1537 and TA1538 incubated with up to 5 mg copper quinolinolate/plate and in *S. typhimurium* TA98 and TA100 incubated with up to 5 mg copper sulfate/plate. Demerec et al. (1951) reported dose-related mutagenic effects in *E. coli* with 2 to 10 ppm copper sulfate in a reverse mutation assay. Negative results were obtained with copper sulfate or copper chloride in assays using *S. cerevisiae* (Singh, 1983) and *Bacillus subtilis* (Nishioka, 1975, Matsui, 1980, Kanematsu et al., 1980). Errors in DNA synthesis from poly(c)templates have been induced in viruses incubated with copper chloride or copper acetate (Sirover and Loeb, 1976). Chromosomal aberrations were induced in isolated rat hepatocytes when incubated with copper sulfate (Sina et al., 1983). Casto et al. (1979) showed enhanced cell transformation in Syrian hamster embryo cells infected with simian adenovirus with the addition of cuprous sulfide and copper sulfate. High concentrations of copper compounds have been reported to induce mitosis in rat ascites cells and recessive lethals in *Drosophila melanogaster*. Law (1938) reported increases in the percent lethals observed in *Drosophila* larvae and eggs when exposed to copper by microinjection (0.1% copper sulfate) or immersion (concentrated aqueous copper sulfate), respectively.

II.B. QUANTITATIVE ESTIMATE OF CARCINOGENIC RISK FROM ORAL EXPOSURE

Not available.

II.C. QUANTITATIVE ESTIMATE OF CARCINOGENIC RISK FROM INHALATION EXPOSURE

Not available.

APPENDIX E

Nickel Refinery Dust; no CASRN

Source: EPA IRIS

The references have been removed from the appendix. They can be found on the EPA IRIS web site.

Health assessment information on a chemical substance is included in IRIS only after a comprehensive review of chronic toxicity data by U.S. EPA health scientists from several Program Offices and the Office of Research and Development. The summaries presented in Sections I and II represent a consensus reached in the review process. Background information and explanations of the methods used to derive the values given in IRIS are provided in the Background Documents.

STATUS OF DATA FOR Nickel refinery dust

Oral RfD Assessment (I.A.)	no data
Inhalation RfC Assessment (I.B.)	no data
Carcinogenicity Assessment (II.)	on-line 01/01/1991

I. CHRONIC HEALTH HAZARD ASSESSMENTS FOR NONCARCINOGENIC EFFECTS

I.A. REFERENCE DOSE FOR CHRONIC ORAL EXPOSURE (RfD)

Not available at this time.

I.B. REFERENCE CONCENTRATION FOR CHRONIC INHALATION EXPOSURE (RfC)

Not available at this time.

II. CARCINOGENICITY ASSESSMENT FOR LIFETIME EXPOSURE

Substance Name -- Nickel refinery dust

CASRN --

Last Revised -- 01/01/1991

Section II provides information on three aspects of the carcinogenic assessment for the substance in question; the weight-of-evidence judgment of the likelihood that the substance is a human carcinogen, and quantitative estimates of risk from oral exposure and from inhalation exposure. The quantitative risk estimates are presented in three ways. The slope factor is the result of application of a low-dose extrapolation procedure and is presented as the risk per (mg/kg)/day. The unit risk is the quantitative estimate in terms of either risk per ug/L drinking water or risk per ug/cu.m air breathed. The third form in which risk is presented is a drinking water or air concentration providing cancer risks of 1 in 10,000, 1 in 100,000 or 1 in 1,000,000. The rationale and methods used to develop the carcinogenicity information in IRIS are described in The Risk Assessment Guidelines of 1986 (EPA/600/8-87/045) and in the IRIS Background Document. IRIS summaries developed since the publication of EPA's more recent Proposed Guidelines for Carcinogen Risk Assessment also utilize those Guidelines where indicated (Federal

Register 61(79):17960-18011, April 23, 1996). Users are referred to Section I of this IRIS file for information on long-term toxic effects other than carcinogenicity.

II.A. EVIDENCE FOR CLASSIFICATION AS TO HUMAN CARCINOGENICITY

II.A.1. WEIGHT-OF-EVIDENCE CLASSIFICATION

Classification -- A; human carcinogen

Basis -- Human data in which exposure to nickel refinery dust caused lung and nasal tumors in sulfide nickel matte refinery workers in several epidemiologic studies in different countries, and on animal data in which carcinomas were produced in rats by inhalation and injection

II.A.2. HUMAN CARCINOGENICITY DATA

Sufficient. Nickel refinery dust from pyrometallurgical sulfide nickel matte refineries is considered a human carcinogen when inhaled. Evidence of carcinogenicity includes a consistency of findings across different countries (Clydach, Wales; Copper Cliff, Ontario; Port Colborne, Ontario; Kristiansand, Norway; and Huntington, WV) in several epidemiologic studies, specificity of tumor site (lung and nose), high relative risks, particularly for nasal cancer, and a dose-response relationship by length of exposure. Excess risks are greatest in the dustier areas of the respective refineries. At Port Colborne, Roberts et al. (1983) reported high risks of lung (SMR = 298) and nasal (SMR = 9412) cancer among men "ever exposed" to calcining, leaching, and sintering, the dustier areas of the refinery. Similar exposures and high risks of lung and nasal cancer were observed in the calcining sheds at Clydach (lung SMR = 510, nasal SMR = 26,667) (Peto et al., 1984), the sintering furnaces at Copper Cliff (lung SMR = 424, nasal SMR = 1583) (Roberts and Julian, 1982), and the roasting/smeltering (lung SMR = 360, nasal SMR = 4000) and electrolysis (lung SMR = 550, nasal SMR = 2700) furnaces at Kristiansand, Norway (Magnus et al., 1982). In the study of refinery and nonrefinery workers at a nickel refinery in West Virginia, nasal cancer was exclusive to the refinery workers, with an SMR of 2443 (Enterline and Marsh, 1982). No large excess of lung cancer was observed in either refinery (SMR = 118) or nonrefinery (SMR = 107.6) employees. The data do show a dose-response relationship between cumulative nickel exposure and lung cancer consistent with findings at nickel refineries in Clydach, Wales (Peto et al., 1984) and Copper Cliff, Ontario (Chovil et al., 1981). While the dust levels and lung cancer relative risks were much higher in the two latter refineries, all dose-response relationships appear linear, and the tumor type and sites are the same, indicating that the functional relationship spans a broad range of nickel exposures.

II.A.3. ANIMAL CARCINOGENICITY DATA

Animal studies indicate that some nickel refinery dusts are potentially carcinogenic. Nickel refinery flue dust (20% nickel sulfate, 59% nickel subsulfide, and 6.3% nickel oxide) from Port Colborne, Canada was tested for carcinogenic potential (Gilman and Ruckerbauer, 1962) by intramuscular injection. It was found to be a strong inducer of injection-site sarcomas in Hooded (52/66) and Wistar (8/20) rats after injection of 20 or 30 mg in one or both thighs and in mice (23/40) after injection of 10 mg/thigh. Fisher et al. (1971), as reviewed by Rigaut (1983), tested nickel refinery dust (20% nickel sulfate,

59% nickel subsulfide, and 6.3% nickel oxide) by inhalation. The refinery dust was one of six types of dust exposures administered to 348 rats at 5 to 15 mg/cu.m. The combined tumor incidence for refinery dust, synthetic dust, nickel subsulfide, and iron sulfide was 11 pulmonary tumors in the 348 rats. When Wistar rats were exposed to a combination of nickel and iron dust at concentrations of 2.1 +/- 0.2 mg Ni/cu.m. and 1.9 +/- 0.2 mg Fe/cu.m (Kim et al., 1976), one of the 60 surviving rats developed lung cancer. An intermediate of nickel refinery dust which contains nickel subsulfide, nickel oxide, and metallic nickel (Feinstein dust) was tested in albino (nonpedigree) rats at 70 mg dust/cu.m, 5 hours/day for 6 months (Saknyn and Blohkin, 1978, as reviewed by Sunderman, 1981). Squamous-cell carcinomas were found in two of the five surviving treated rats. Saknyn and Blohkin (1978) also treated the Albino rats by intraperitoneal injection of Feinstein dust at 90 to 150 mg/rat. Six of the 39 survivors developed injection-site sarcomas.

Nickel dust from roasting (31% nickel subsulfide and 33.4% nickel oxide + silicon oxide and oxides of iron and aluminum) was tested for carcinogenicity in rats by inhalation (Belobragina and Saknyn, 1964, as reviewed by Rigaut, 1983). After exposure to 80 to 100 mg/cu.m, 5 hours/day for 12 months, no tumors were found. Three carcinogenicity studies (Schroeder and Mitchener, 1975; Schroeder et al., 1964, 1974) of nickel acetate and an unspecified nickel salt using doses of 5 ppm of nickel in the drinking water of Long-Evans rats and Swiss mice produced negative results. Ambrose et al. (1976) administered nickel sulfate hexahydrate in the diet of Wistar-derived rats and beagle dogs for 2 years at nickel concentrations of 100 to 2500 ppm. A lack of carcinogenic response was observed in both studies. The dog study may have been inadequate to detect a carcinogenic response, since the duration was relatively short.

II.A.4. SUPPORTING DATA FOR CARCINOGENICITY

Nickel refinery dust has not been studied using in vitro short-term test systems or tests for macromolecular interactions.

II.B. QUANTITATIVE ESTIMATE OF CARCINOGENIC RISK FROM ORAL EXPOSURE

Not available.

II.C. QUANTITATIVE ESTIMATE OF CARCINOGENIC RISK FROM INHALATION EXPOSURE

II.C.1. SUMMARY OF RISK ESTIMATES

Inhalation Unit Risk -- 2.4E-4 per (ug/cu.m)

Extrapolation Method -- Additive and multiplicative

Air Concentrations at Specified Risk Levels:

Risk Level	Concentration
-----	-----
E-4 (1 in 10,000)	4E-1 ug/cu.m
E-5 (1 in 100,000)	4E-2 ug/cu.m
E-6 (1 in 1,000,000)	4E-3 ug/cu.m

II.C.2. DOSE-RESPONSE DATA FOR CARCINOGENICITY, INHALATION EXPOSURE

Estimates of Incremental Unit Risks for Lung Cancer due to Exposure to 1 ug Ni/cu.m for a Lifetime Based on Extrapolations from Epidemiologic Data Sets Study
Relative Risk Model Huntington, WV (Enterline and Marsh, 1982) (maximum likelihood estimates only)

Refinery workers	1.5E-5 - 3.1E-5
Nonrefinery workers	9.5E-6 - 2.1E-5
Copper Cliff, Ontario (Chovil et al., 1981)	1.1E-5 - 8.9E-5
Clydach, Wales (Peto et al., 1984)	8.1E-5 - 4.6E-4
Kristiansand, Norway (Magnus et al., 1982)	1.9E-5 - 1.9E-4
Midpoint of range for refinery workers	2.4E-4

II.C.3. ADDITIONAL COMMENTS (CARCINOGENICITY, INHALATION EXPOSURE)

Nickel refinery dust is a mixture of many nickel moieties, and it is not certain what the carcinogenic nickel species is in the refinery dust.

Data sets from nickel refineries in Huntington, WV (Enterline and Marsh, 1982), Copper Cliff, Ontario (Chovil et al., 1981), Clydach, Wales (Peto et al., 1984), and Kristiansand, Norway (Magnus et al., 1982) provide information available for choice of model or for separation of risk by the type of nickel exposure. The dose-response curves for nasal cancer were not used for risk estimation because nasal cancer risk from nickel is thought to be an occupational hazard associated only with the pyrometallurgical process, and these tumors are not found in the general public to the same extent as lung tumors. The same lung tumor type was found in all epidemiologic studies of occupational exposure to nickel refinery dust. The average relative risk model was applied to the Huntington, WV and Copper Cliff, Ontario data sets.

For the four data sets analyzed, both the additive and multiplicative excess risk models were fitted whenever possible. The relative risk or multiplicative model follows the assumption that the background cause-age-specific rate at any time is increased by an amount proportional to the cumulative dose up to that time. The model assumes the standardized mortality ratio (SMR) is linearly related to dose and is constant for a set cumulative exposure. Excess mortality for a set cumulative exposure is constant over time, and excess risk remains constant once exposure ceases. The relative risk model differs from the additive risk model in that the latter model assumes that the excess cause-age-specific rate is increased by an amount proportional to the cumulative exposure up to that time.

The unit risk estimates ranged from 1.1E-5 to 4.6E-4 per (ug/cu.m). The estimates from the Huntington refinery were somewhat lower, but this may be a result of only the small sample size. If the nasal cancer deaths are added to the eight lung cancer deaths, the unit risk estimate becomes 1.3E-4 per (ug/cu.m), well within the range of the other estimates. As the best estimate, the midpoint of the range, 2.4E-4 per (ug/cu.m), is taken as the incremental unit risk due to a lifetime exposure to nickel matte refinery dust.

When the additive risk model is applied to the data for Huntington, WV, the estimates (2.8E-4 and 1.8E-4 for refinery and nonrefinery workers, respectively) are close to those

derived by the relative risk model. The above unit risk should not be used if the air concentration exceeds 40 ug/cu.in, since above this concentration the unit risk may not be appropriate.

II.C.4. DISCUSSION OF CONFIDENCE (CARCINOGENICITY, INHALATION EXPOSURE)

Four data sets, all from humans, offer a range of incremental unit risk estimates that are consistent with each other.

APPENDIX F

Zinc and Compounds

Source: EPA IRIS
CASRN 7440-66-6

The references have been removed from the appendix. They can be found on the EPA IRIS web site.

I. CHRONIC HEALTH HAZARD ASSESSMENTS FOR NONCARCINOGENIC EFFECTS

I.A. REFERENCE DOSE FOR CHRONIC ORAL EXPOSURE (RfD)

The oral Reference Dose (RfD) is based on the assumption that thresholds exist for certain toxic effects such as cellular necrosis. It is expressed in units of mg/kg-day. In general, the RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. Please refer to the Background Document for an elaboration of these concepts. RfDs can also be derived for the noncarcinogenic health effects of substances that are also carcinogens. Therefore, it is essential to refer to other sources of information concerning the carcinogenicity of this substance. If the U.S. EPA has evaluated this substance for potential human carcinogenicity, a summary of that evaluation will be contained in Section II of this file.

NOTE: This RfD for the soluble salts of zinc supplies adequate zinc to meet the requirements in adolescents and adults over a lifetime without any concurrent physiological impairment. It does not supply the Recommended Daily Allowance (RDA) to those members of the population who have greater requirements for a short, less-than-lifetime duration, for example, infants, pre-adolescent children, or, possibly, lactating women. For short-term requirements in infants, pre-adolescent children, and lactating females, refer to the RDAs (NRC, 1989).

At a Workshop on the "Risk Assessment of Essential Elements" (Herndon, VA; March 10-12, 1992), several nutritionists commented on the derivation of the zinc RfD. The most relevant comment raised the issue of zinc bioavailability from various media. Dr. Harold Sandstead (1992) summarized this viewpoint and suggested the following values for zinc RfDs from various media: zinc supplements - 0.25 mg/kg/day; "omnivores" - 0.7 mg/kg/day; and vegetarians - 1.7 mg/kg/day. The proposed RfD for individuals consuming supplements, which is roughly comparable to soluble salts of zinc, is quite similar to the RfD verified by EPA's RfD/RfC Work Group. This agreement between the nutritionists and the toxicologists gives the EPA greater confidence in the verified RfD.

I.A.1. ORAL RfD SUMMARY

Critical Effect	Experimental Doses*	UF	MF	RfD
47% Decrease in	NOAEL: None	3	1	3E-1

erythrocyte superoxide
dismutase (ESOD) mg/kg/day
LOAEL = 59.72 mg/day

concentration in adult females after 10 weeks of zinc exposure (1.0 mg/kg/day)

Human Diet Supplement Study

*Conversion Factors: The dose conversion factors were based on a 60-kg reference female body weight. Total dose was derived from estimations from the FDA Total Diet Study for 1982-1986, plus reported supplemental dose. For example, for the Yadrick et al., 1989 study, the dose is 1.0 mg/kg-day based on 50 mg zinc supplement plus 9.72 mg/day zinc from the diet (total of 60), divided by the assumed average body weight of the participants (60 kg).

I.A.2. PRINCIPAL AND SUPPORTING STUDIES (ORAL RfD)

Yadrick, M.K., M.A. Kenney and E.A. Winterfeldt. 1989. Iron, copper, and zinc status: Response to supplementation with zinc or zinc and iron in adult females. *Am. J. Clin. Nutr.* 49: 145-150.

The oral RfD is based on a clinical study that investigated the effects of oral zinc supplements on copper and iron balance. This study is supported by several other studies which indicate that zinc supplementation can alter copper balance. The effects on copper and iron biochemistry are considered of concern since long-term iron or copper deficiency could result in significant adverse effects. For example, zinc supplementation therapy with megadoses of up to 5 g/day, as well as smaller amounts of 150 mg/day, taken for 1 to 2 years have produced copper deficiency anemia (Fischer et al., 1984). In addition, several studies have investigated the effects of zinc supplementation on the high-density lipoprotein (HDL) levels of adult males.

These have been added as supporting studies because the observed change in HDL values in males may be significant since a sustained decrease in HDL concentrations may be associated with increased risk of coronary artery disease when combined with a parallel increase in low-density lipoprotein (LDL) cholesterol. A 10-week study of zinc supplementation in 18 healthy women given zinc gluconate supplements twice daily (50 mg zinc/day, or 1.0 mg/kg-day, see below) resulted in a decrease of erythrocyte superoxide dismutase (ESOD) activity (Yadrick et al., 1989). ESOD concentrations declined over the 10-week supplementation period and at 10 weeks were significantly different ($p < 0.05$) from values during the pretreatment period. By 10 weeks, ESOD activity had declined to 53% of pretreatment levels. Change in enzyme activity is considered a better indicator of altered copper status than a measure of metal concentration in tissue or plasma. This has been documented by studies in rats fed copper-deficient or high-zinc diets, in which copper metalloenzyme activity is greater and precedes changes in plasma or tissue levels of copper (L'Abbe and Fischer, 1984a,b). Ceruloplasmin concentrations were not altered. Serum zinc was significantly increased. There was also a significant decline in serum ferritin and hematocrit values at 10 weeks. Such a decrease could pose a significant risk to the iron status of women.

No measurements were made of dietary zinc or copper in this study. However, a level of dietary zinc can be estimated at 9.72 mg/day for females (20- to 30-years old) from the results of the FDA Total Diet Study for 1982-1986 (Pennington et al., 1989). The

LOAEL of 1.0 mg/kg-day was calculated from the sum of these dietary estimates and the supplemental zinc dose using an assumed body weight of 60 kg for adult females, as shown in the conversion factor section.

Support for considering the intake of 50 mg/kg-day supplemental zinc as a threshold LOAEL is provided by Fischer et al. (1984) which also suggests that zinc affects copper balance at doses of 0.95 mg/kg-day in males. Healthy men given 25 mg of zinc as gluconate twice daily for a 6-week period displayed a significant decrease ($p < 0.05$) in erythrocyte superoxide dismutase (ESOD) activity at the end of 6 weeks exposure. There were no differences between serum copper levels or ceruloplasmin activity in the 13 members of the supplement group compared with controls. Serum zinc levels were significantly increased in the supplement group after 2 weeks.

Prasad et al. (1978) fed a patient with sickle cell anemia supplements of 150 to 200 mg zinc/day for 2 years. The supplement resulted in copper deficiency; serum copper and plasma ceruloplasmin levels were decreased. When copper was administered, the plasma ceruloplasmin levels became normal. In a follow-up study, of 13 patients on zinc therapy (similar treatment levels assumed), 7 patients had ceruloplasmin levels at the lower limit of normal after 24 weeks of dosing.

In a 9-week study, Festa et al. (1985) fed nine male students diets containing 2.6 mg copper/day and 1.8-20.7 mg zinc/day for 1- to 2-week periods. This study indicated that fecal copper excretion was influenced by the amount of zinc in the diet and the length of time it was administered. Typically, after 1-2 weeks at 18.5 mg/day (just 3.5 mg/day higher than the adult RDA), subjects lost significantly more copper in the feces. Plasma copper concentrations were unchanged. Groups of 9, 13 or 9 healthy white men were administered 0, 50, or 75 mg/kg-day zinc as zinc gluconate, respectively, for 12 weeks (Black et al., 1988). The subjects were given instructions to avoid foods high in calcium, fiber and phytic acid, dietary constituents that have a negative impact on zinc absorption. Subjects were also told to restrict their intake of zinc-rich foods in order to minimize the variation in daily dietary zinc. Three-day dietary records were collected on a biweekly basis. These records indicated that the dietary zinc intakes of the three treatment groups were 12.5, 14.0, and 9.5 mg/day for the groups receiving 0, 50, and 75 mg/kg-day supplement, respectively. Based on the average body weights for each treatment group, these doses correspond to a total zinc intake of 0.16, 0.85, and 1.10 mg/kg-day.

Biweekly blood samples were collected from all subjects and analyzed for total cholesterol, HDL-cholesterol, LDL-cholesterol, triglycerides, zinc, and copper. Urinary zinc and copper values were also determined. There was a general decline in the mean serum HDL-cholesterol for the 75-mg supplement group between weeks 6 and 12. HDL values for this group were significantly lower than those for the placebo group at weeks 6 and 12 ($p < 0.05$). When the mean HDL-cholesterol level of these subjects was compared to population percentile norms, there was a decline from the 92nd to the 77th percentile (Simko et al., 1984) in 6 weeks, followed by a relative stabilization of HDL values for the remaining 6-week test period. There was also a decline in the HDL values for the 50-mg group between weeks 8 through 12; however, this decline was not significantly different ($p \geq 0.05$) from that for the controls until the 12th week of treatment. Over the 12-week period the HDL values for the 50-mg group declined from the 90th to the 77th population percentile norms. Serum zinc, copper, total cholesterol,

LDL-cholesterol and triglycerides did not appear to be affected by treatment. While it is not absolutely certain that the 50-mg zinc/day supplement represents a clearly biologically significant endpoint, this level, when viewed collectively with other studies investigating effects on HDL-cholesterol, may signify the beginning of the dose-response trend. The significance of this change is unknown in light of an absence of increase in LDLs.

Zinc supplementation (160 mg as zinc sulfate) was found to lower HDL-cholesterol values in 11 healthy men when administered over 5 weeks (Hooper et al., 1980). A control group of eight subjects received a placebo. Fasting cholesterol, HDL-cholesterol, and triglycerides were determined on a weekly basis for 7 weeks and again 11 weeks after the end of supplementation. Dietary zinc levels were not measured; however, in the FDA Total Diet Study, adult males consumed an average of 16.41 mg/day during 1982-1987 (Pennington et al., 1989). Based on a 70-kg average body weight and 16.41 mg/day dietary zinc, the average dietary zinc intake for those receiving a supplement was 2.52 mg/kg-day.

After an initial HDL increase during the first 2 weeks of supplementation, HDL levels were significantly lower than those for the controls during weeks 4 through 7 ($p = 0.002$ to 0.0001). HDL levels returned to normal 11 weeks after supplementation had ended. The 11 subjects of this study had initial mean HDL values below average for their age category (23-35 years old). During the first 7 weeks of monitoring, their HDL percentile values fell from the 36th to the 8th population percentile norm. Percentile standings lower than 10 are associated with cardiovascular risk. Serum cholesterol, LDL-cholesterol, and triglycerides did not change significantly during the study; serum zinc levels increased during the supplementation period. Serum cholesterol values were normal. A third study of the effects of zinc supplementation was conducted by Chandra (1984) in 11 adult men (ages not given). Zinc sulfate tablets were administered twice daily for a total zinc supplement intake of 300 mg/day.

Average dietary zinc during the supplementation period was 10.1 mg/day, based on 24-hour recall data and 11.2 mg/day in the pre-test period. Thus, the daily zinc intake was 4.43 mg/kg-day for a 70-kg male during supplementation.

Fasting serum cholesterol, HDL-cholesterol, LDL-cholesterol, and triglycerides were measured biweekly for 6 weeks; a final measurement of these parameters was conducted at 16 weeks. Total lymphocytes, T-lymphocytes, and B-lymphocytes were also measured. Lymphocyte activity was monitored through polymorphonuclear migration response to chemotactic phytohemagglutinin (PHA) stimulation and phagocytosis of opsonized bacteria.

There was a significant decrease in serum HDL values during weeks 4 and 6 ($p < 0.1$ and $p < 0.01$, respectively) with a return to baseline levels at week 16 (Chandra, 1984). LDL-cholesterol levels were significantly increased ($p < 0.05$) at week 6, but there were no significant changes in serum cholesterol and triglycerides. During the 6-week supplement administration period, the HDL percentile values fell from the 43rd to the 6th percentile, as estimated from the population percentile norms for 30- to 35-year-old males (Simko et al., 1984).

There were no significant changes in lymphocyte counts during the period of zinc supplementation, but polymorphonuclear response to PHA stimulation (chemotactic

migration) and phagocytosis were impaired (Chandra, 1984). Plasma zinc values increased during the supplement administration.

I.A.3. UNCERTAINTY AND MODIFYING FACTORS (ORAL RfD)

UF -- An uncertainty factor of 3 was used, based on a minimal LOAEL from a moderate-duration study of the most sensitive humans and consideration of a substance that is an essential dietary nutrient.

MF -- None

I.A.4. ADDITIONAL STUDIES / COMMENTS (ORAL RfD)

Zinc is an essential nutrient with RDA values ranging from 5 to 15 mg/day for different age and sex categories (NRC, 1989). The RDA is an estimate of the zinc needed for growth, development, metabolism and tissue maintenance for over 98% of the healthy American population. For 79% of a 70-year lifetime (55 years), the proposed RfD of 0.3 mg/kg-day supplies adequate zinc to meet these requirements in adolescents and adults without any concurrent physiological impairment. It does not supply the RDA for infants, preadolescent children or, possibly, for lactating women. The RfD of 0.3 mg/kg-day is expected to be without adverse effects when consumed on a daily basis over an extended period of time. It neither induces a nutritional deficiency in healthy, non-pregnant, adult humans consuming the average American diet nor causes undesirable inhibition of normal lipid transport.

When the three studies monitoring HDL-cholesterol are considered as a group, they show a consistent lowering of HDL-cholesterol levels in response to the addition of zinc to the diet, an effect that is reversed with cessation of the zinc supplementation. The data of Black et al. (1988) indicate that the depressed HDL values can persist for up to 12 weeks. Data are available from all 3 studies at 6 weeks. However, in the Hooper et al. (1980) study, the 6-week data represent HDL status 1 week after supplement administration ended. Additional data will be needed to clarify whether or not this change is significant with longer exposure.

Supplemental zinc does not appear to have the same effect on females that it has on males. Healthy adult females were given supplemental zinc doses of 0, 15, 50 or 100 mg/day zinc as zinc acetate for 60 days (Freeland-Graves et al., 1982). Plasma cholesterol, HDL-cholesterol, and zinc were monitored at biweekly intervals. A transitory decrease in HDL values was noted at 4 weeks, but only in the group receiving the 100-mg/day supplement (1.8 mg/kg-day based on a 60-kg body weight and 8.1 mg/day zinc in the diet [from diet records]). This decrease in HDL values was not apparent at 6 and 8 weeks. Serum zinc levels were also highest in these subjects at 4 weeks.

A very slight but statistically significant ($p = 0.04$) 2-mg/dL increase in HDL cholesterol was seen in a group of 22 elderly male and female subjects (sex ratio unknown) 8 weeks after they ceased using zinc supplements (Goodwin et al., 1985). Serum zinc values fell from 92 to 86 $\mu\text{g/dL}$ during the same period. The average supplement intake was 29.1 mg/day with a range of 17.5 to 52.2 mg/day. The increase in HDL value seemed to be greatest for the subjects with the highest ratings for physical activity. Although the data in this study are far from conclusive with regard to the relationship between zinc and

HDL values, they do add to the weight of evidence, which suggests that the impact of supplemental zinc on HDL levels is real.

I.A.5. CONFIDENCE IN THE ORAL RfD

Study -- Medium

Data Base -- Medium

RfD -- Medium

The level of confidence in the studies is medium since they are well- conducted clinical studies with many biochemical parameters investigated but only few numbers of humans were tested. The confidence in the overall database is medium since these studies are all of short duration. Medium confidence in the RfD follows.

I.B. REFERENCE CONCENTRATION FOR CHRONIC INHALATION EXPOSURE (RfC)

Not available at this time.

II. CARCINOGENICITY ASSESSMENT FOR LIFETIME EXPOSURE

II.A. EVIDENCE FOR CLASSIFICATION AS TO HUMAN CARCINOGENICITY

II.A.1. WEIGHT-OF-EVIDENCE CLASSIFICATION

Classification -- D; not classifiable as to human carcinogenicity

Basis -- Based on inadequate evidence in humans and animals.

II.A.2. HUMAN CARCINOGENICITY DATA

Inadequate. There are no reports on the possible carcinogenicity of zinc and compounds per se in humans. Case studies have been used to evaluate the effects of zinc administered for therapeutic reasons. There are reports, which compare zinc levels in normal and cancerous tissue. Studies of occupational exposure to zinc compounds have also been conducted, but have limited value because they do not correlate exposure with cancer risk. Case reports of chronic therapeutic exposure for approximately 2 years of two patients, a 59-year-old female and a 26-year-old homozygous sickle-cell male, to 100-150 mg/day zinc as zinc sulfate or zinc acetate, respectively, have reported a profound anemia associated with hypoceruloplasminemia and hypocupremia (Porter et al., 1977; Prasad et al., 1978). The conditions were corrected by copper supplementation and, in one case, withdrawal of zinc.

Habib et al. (1976) reported that average zinc concentrations in normal and hypertrophic prostate tissues were similar, approximately 6.8 $\mu\text{mol/g}$, but the average zinc concentration was lower in carcinomatous prostate tissues (2.6 $\mu\text{mol/g}$). These tissue samples were obtained as follows: normal prostate tissues were obtained at autopsy from 9 men 25-58 years old (average age 36); and both hyperplastic and carcinomatous prostate tissues were obtained from the biopsies of 23 men 58-87 years old (average age 70) and from 9 men 64-91 years old (average age 73), respectively. Several other studies have also shown lower average zinc concentrations in cancerous vs. normal or hypotrophic prostate tissue (U.S. EPA, 1987). NRC (1978) and U.S. EPA (1987) have reviewed other studies, which have noted both high and low zinc levels in other cancerous and noncancerous tissues with no definite pattern. From these studies it could not be concluded whether zinc was a carcinogen.

Several occupational studies have been conducted on workers exposed to zinc compounds (Batchelor et al., 1926; Chmielewski et al., 1974a,b; Bobrishchev-Pushkin et al., 1977). No increase in the incidence of cancer was noted; however, the studies were designed to evaluate other endpoints and did not specifically address cancer. Other symptoms such as slight leukocytosis, occurrences of metal fume fever, respiratory disease and hypocalcemia were some of the findings noted in exposed workers. Batchelor et al. (1926) extensively investigated workers exposed to zinc in a smelter. A total of 24 workers whose exposure ranged from 2-35.5 years were selected. In most work areas the mean zinc concentrations were generally below 35 mg/cu.m, except in the zinc dust plant where concentrations of up to 130 mg/cu.m were measured. The average level of zinc in whole blood of the 24 exposed workers was 458 ug/100 mL, compared with 387 ug/100 mL in 10 control measurements. No information was given about the control subjects. Klucik and Koprda (1979) found that exposure levels to zinc oxide dust in a zinc oxide factory were on average 0.5 mg/cu.m for zinc melters and 2.44-7.15 mg/cu.m for zinc oxide packers; it was not indicated how these values were obtained. Chmielewski et al. (1974a,b) examined a group of workers who were exposed to zinc oxide in a shipyard; this included 20 ship smiths, 20 electric welders, 20 ship's pipeline fitters, and 20 zincifying workers. High concentrations of zinc oxide were found at the stands of the electric welders, who worked in containers (maximum 58 mg/cu.m, mean 18 mg/cu.m), and the ship smiths, who worked in a superstructure (maximum 50 mg/cu.m, mean 12 mg/cu.m). These workers were also exposed to other hazardous compounds, such as nitrogen oxides. Bobrishchev-Pushkin et al. (1977) studied 1018 workers in the casting shops of three copper alloy production facilities in the USSR. Four hundred and fifty-one workers from the rolling shops were used as controls. The average level of zinc oxide exposure in the casting shop was 2.1 mg/cu.m (range of 0.2-5.1 mg/cu.m), well below the USSR's maximally allowable concentration of 6 mg/cu.m. Workers were also exposed to other metals such as copper, lead and nickel.

II.A.3. ANIMAL CARCINOGENICITY DATA

Inadequate. In a 1-year study, an unspecified number of newborn Chester Beatty stock mice (sex not reported) were administered 0, 1000, or 5000 ppm zinc (approximately 0, 170, or 850 mg/kg/day) as zinc sulfate in drinking water (Walters and Roe, 1965). A separate group of mice received zinc oleate in the diet at an initial dose of 5000 ppm zinc; this dose was reduced to 2500 ppm after 3 months and to 1250 ppm after an additional 3 months because of mortality due to anemia. An epidemic of ectromelia caused the deaths of several mice during the first 8 weeks; consequently, additional control and test-diet groups were established. There was no difference in body weight gain between control and treated groups, except the dietary zinc group, which became anemic. Survival was not reported in treated compared with control groups. An apparent increase in the incidence of hepatomas was observed in treated mice surviving for 45 weeks or longer relative to controls (original and replacement mice pooled). The hepatoma incidence in the control, low-dose drinking water, high-dose drinking water, and test-diet group was 3/24 (12.5%), 3/28 (10.7%), 3/22 (13.6%), and 7/23 (30.4%), respectively. Incidence of malignant lymphoma in the control, low-dose drinking water, high-dose drinking water, and test-diet groups was 3/24 (12.5%), 4/28 (14.3%), 2/22 (9%), and 2/23 (8.7%), respectively. Incidence of lung adenoma in the control, low-dose drinking water, high-

dose drinking water, and test-diet groups was 10/24 (41.7%), 9/28 (32.1%), 5/22 (22.7%), and 9/23 (39.1%), respectively. None of these were significantly elevated in a statistical analysis of this data performed by the EPA. In a 14-month study conducted with 150 C3H mice (sex not reported), administration of 500 mg/L zinc sulfate (approximately 100 mg/kg/day) in the drinking water resulted in hypertrophy of the adrenal cortex and pancreatic islets (Aughey et al., 1977). No tumors were noted; however, only the adrenal, pancreas and adenohypophysis were examined. Accurate consumption data could not be obtained due to spillage during drinking. No instances of adrenal or pancreatic hypertrophy were seen in a control group (number of animals not stated) that received only distilled water.

After an intratesticular injection of zinc, Guthrie observed seasonally-related testicular tumors in fowl (Guthrie, 1964) but no tumors in rats (Guthrie, 1956). Guthrie (1964) administered zinc chloride, zinc acetate or zinc stearate to groups of white leghorn chickens by intratesticular injection (approximately 0.01 g/injection); groups of chickens were sacrificed from 3 weeks to 11 months. Eight of the 111 chickens injected with zinc chloride in January and February developed testicular testoma, while none of the 48 chickens injected with zinc chloride in March developed tumors. None of the 36 chickens injected with zinc acetate in March and none of the 14 chickens injected with zinc stearate in January and February developed tumors; no conclusions about the carcinogenicity of these two compounds could be made because an insufficient number of chickens were tested. No control group was described.

Guthrie injected 0.15-0.20 mL of 10% zinc sulfate into the testis of nineteen 4-month-old rats and 0.15 mL of 5% zinc chloride into the testis of twenty-nine 3-month-old rats (strain not specified) (Guthrie 1956). No testicular tumors were observed in either group at sacrifice 15 months after injection. No controls were described. Riviere et al. (1959) injected 5% zinc chloride in distilled water into the testicles of 100 Wistar rats. The rats were subdivided into several groups; some rats were unilaterally castrated and some rats received an injection of 200 units serum gonadotrophin and a subcutaneous implantation of a 25 mg pellet of distilbene or 100 mg testosterone. The number of rats in each of the four groups (unilateral castration +/- hormone treatment and untreated +/- hormone treatment was not stated. No control group was described. Testicular tumors (including interstitial tumors, a seminoma and an embryoma) became apparent 15 months after inoculation (tumor incidence not specified). There are no specific data on the effects of hormones in this experiment.

Halme (1961) exposed tumor-resistant and tumor-susceptible strains of mice to zinc in drinking water. In a 3-year, five-generation study, zinc chloride was added to the water of tumor-resistant mice (strain not specified); the groups received 0, 10, 20, 50, 100, or 200 mg Zn/L. The spontaneous tumor frequency for this strain of mice was 0.0004%. The tumor frequencies in the generations were: F0=0.8%, F1=3.5%, F1 and F2=7.6% and F3 and F4=25.7%. Most of the tumors occurred in the 10 and 20 mg Zn dose groups. No statistical analyses and no individual tumor-type data were reported. In the tumor susceptible mice, strains C3H and A/Sn received 10-29 mg Zn/L in their drinking water for 2 years; 33/76 tumors were observed in the C3H strain (31 in females) and 24/74 tumors were observed in the A/Sn strain (20 in females). Most of the tumors were adenocarcinomas. The numbers of specific tumor types were not reported. The tumor frequencies (43.4% for C3H and 32.4% for A/Sn both sexes combined) were higher than

the spontaneous frequency (15% for each strain), although no statistical analyses were reported.

II.A.4. SUPPORTING DATA FOR CARCINOGENICITY

In a short-term, in vivo assay, Stoner et al. (1976) injected strain A/Strong mice (20/sex/dose) intraperitoneally with zinc acetate 3 times/week for a total of 24 injections (total doses were 72, 180, or 360 mg/kg). Controls (20/sex/group) consisted of an untreated group, a vehicle control group administered 24 injections of saline and a positive control group administered a single injection of urethan (20 mg/mouse). Mice were sacrificed 30 weeks after the first injection; survival was comparable for all groups. There was no increase in number of lung tumors per mouse in treated animals relative to the pooled controls. While four thymomas were observed in zinc acetate-treated groups and none in controls, the occurrence of these tumors was not statistically significantly elevated.

Urine samples from subjects occupationally exposed in the rubber industry to a variety of compounds, including zinc oxide, were not found to be mutagenic in the microtitre fluctuation assay with *Salmonella typhimurium* strains TA1535, TA98 and TA100 (Crebelli et al., 1985).

The results of short-term genotoxicity assays for zinc are equivocal. Zinc acetate and/or zinc 2,4-pentanedione have been analyzed in four short-term mutagenicity assays (Thompson et al., 1989). In the *Salmonella* assay (with or without hepatic homogenates), zinc acetate was not mutagenic over a dose range of 50-7200 ug/plate but zinc 2,4-pentanedione was mutagenic to strains TA1538 and TA98 at 400 ug/plate. The addition of hepatic homogenates diminished this response in a dose-dependent manner. In the mouse lymphoma assay, zinc acetate gave a dose-dependent positive response with or without metabolic activation; the mutation frequency doubled at 10 ug/mL. In the CHO in vitro cytogenetic assay, zinc acetate gave a dose-dependent positive response with or without metabolic activation, but the presence of hepatic homogenates decreased the clastogenic effect. Neither zinc acetate nor zinc 2,4-pentanedione were positive in the unscheduled DNA synthesis assay in rat hepatocytes over a dose range of 10-1000 ug/mL.

Zinc chloride is reported to be positive in the *Salmonella* assay (Kalinina et al., 1977), negative in the mouse lymphoma assay (Amacher and Paillet, 1980), and a weak clastogen in cultured human lymphocytes (Deknuddt and Deminatti, 1978). Zinc sulfate is reported to be not mutagenic in the *Salmonella* assay (Gocke et al., 1981), and zinc acetate is reported to not induce chromosomal aberrations in cultured human lymphocytes (Gasiorek and Bauchinger, 1981). Crebelli et al. (1985) found zinc oxide (99% purity) (1000-5000 ug/plate) to be not mutagenic for *Salmonella* in the reversion assay.

Responses in mutagenicity assays are thought to depend on the form (e.g., inorganic or organic salt) of the zinc tested. For example, inorganic salts tend to dissociate and the zinc becomes bound with culture media constituents. Salts that dissociate less readily tend to be transported into the cell and are postulated to cause a positive response (Thompson et al., 1989). Zinc is an essential trace element involved in numerous biological functions including growth, taste and spermatogenesis. It is a cofactor for several enzymes such as those involved in the metabolism of proteins and nucleic acids. Zinc may be a modifier of the carcinogenic response; zinc deficiency or excessively high

levels of zinc may enhance susceptibility to carcinogenesis, whereas supplementation with low to moderate levels of zinc may offer protection (Woo et al., 1988). Zinc deficiency enhanced carcinomas of the esophagus induced by methylbenzyl nitrosoamine (Fong et al., 1978) but retarded the development of cancer of the oral cavity induced by 4-nitroquinoline-N-oxide (Wallenius et al., 1979). In a study that examined both zinc deficiency and supplementation, Mathur (1979) found that animals with a deficient diet (5.9 mg/kg) and animals diet supplemented with excessively high levels of zinc in the diet (200-260 mg/kg) had fully developed carcinomas of the palatal mucosa. While the rats were on the specific diets, the palatal mucosa was painted with 4 nitroquinoline 3 times/week for 20 weeks. In the zinc deficient group 2/25 rats developed cancer of the palatal mucosa; 2/25 rats in the excessive zinc group also developed this form of cancer. Animals supplemented with moderate levels of zinc in the diet (50 mg/kg) developed only moderate dysplasia. Thus, zinc's modifying effect on carcinogenesis may be dose-dependent.

II.B. QUANTITATIVE ESTIMATE OF CARCINOGENIC RISK FROM ORAL EXPOSURE

None.

II.C. QUANTITATIVE ESTIMATE OF CARCINOGENIC RISK FROM INHALATION EXPOSURE

None.

APPENDIX G



MATERIAL SAFETY DATA

FOR ANY EMERGENCY, CALL OCEAN(R) EMERGENCY PHONE(24H):	1-888-289-1911
FOR ALL TRANSPORTATION ACCIDENTS, CALL CHEMTREC@:	1-800-424-9300
FOR ALL MSDS QUESTIONS, CALL CORPORATE DIRECTOR:EH&S:	1-423-336-4007

PRODUCT NAME: WINCHESTER® FRANGIBLE BULLETS

I. PRODUCT AND COMPANY IDENTIFICATION

REVISION DATE: 08-23-1999 SUPERCEDES: 06-17-1999
MSDS NO: 01960-0001 - DPE100000

MANUFACTURER: OLIN CORPORATION 501 Merritt 7 PO Box 4500 Norwalk, CT 06856-4500

SYNONYMS: None

CHEMICAL FAMILY: Mixture

FORMULA: Not Applicable/Mixture

USE DESCRIPTION: Centerfire Ammunition Projectile

OSHA HAZARD CLASSIFICATION: Not considered hazardous, per 29 CFR 1910.1200

SECTION 2 COMPONENT DATA

PRODUCT COMPOSITION

CAS or CHEMICAL NAME: Tungsten powder

CAS NUMBER: 7440-33-7

PERCENTAGE RANGE: Proprietary

HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)

EXPOSURE STANDARDS:

	OSHA (PEL)		ACGIH (TLV)	
	ppm	mg/cubic-meter	ppm	mg/cubic-meter
TWA:	None			5
CEILING:	None		None	
STEL:	None			10

CAS or CHEMICAL NAME: Copper powder

CAS NUMBER: 744-50-8

PERCENTAGE RANGE: Proprietary

HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)

EXPOSURE STANDARDS:

	OSHA (PEL)		ACGIH (TLV)	
	ppm	mg/cubic-meter	ppm	mg/cubic-meter
TWA:		1 (dust) 0.1 (fume)		1 (dust) 0.2 (fume)
CEILING:	None		None	
STEL:	None		None	

CAS or CHEMICAL NAME: Nylon
CAS NUMBER: Supplier proprietary
PERCENTAGE RANGE: Proprietary
HAZARDOUS PER 29 CFR 1910.1200: No
EXPOSURE STANDARDS: None Established

CAS or CHEMICAL NAME: Zinc stearate
CAS NUMBER: 557-05-1
PERCENTAGE RANGE: < 8%
HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust)
EXPOSURE STANDARDS:

	OSHA (PEL)		ACGIH (TLV)	
	ppm	mg/cubic-meter	ppm	mg/cubic-meter
TWA:		15 (total dust) 5 (respirable fraction)		10
CEILING:	None		None	
STEL:	None		None	

CAS or CHEMICAL NAME: Additives
CAS NUMBER: Supplier proprietary
PERCENTAGE RANGE: < 2%
HAZARDOUS PER 29 CFR 1910.1200: No
EXPOSURE STANDARDS: None Established

NOTE: At the high temperatures (< 220 Deg.C) involved in molding the bullets, most of the last three constituents volatilize off and are largely lost in the final product.

SECTION 3 PRECAUTIONS FOR SAFE HANDLING AND STORAGE

AVOID CONTACT OF DUST OR FUME WITH SKIN EYES OR CLOTHING. UPON CONTACT WITH SKIN OR EYES WASH OFF WITH WATER. AVOID BREATHING DUST.

STORAGE CONDITIONS:

No special precautions needed with the bullets other than those normally associated with handling ammunition.
OTHER: Maintain good housekeeping practices in firing ranges to prevent the accumulation of bullet debris, particularly dust. Use cleanup methods, which minimize dust formation.

PRODUCT STABILITY AND COMPATIBILITY

SHELF LIFE LIMITATIONS: None known
INCOMPATIBLE MATERIALS FOR STORAGE OR TRANSPORT: None known

SECTION 4 PHYSICAL DATA

APPEARANCE: Molded brown plastic bullets
MELTING POINT: 185-220 Deg.C (365-428 Deg.F)
BOILING POINT: Nylon decomposes above about 300 Deg.C (572 Deg.F)
DECOMPOSITION TEMPERATURE: > 300 Deg.C (> 572 Deg.F)
SPECIFIC GRAVITY: > 5.0
BULK DENSITY: No Data
pH @ 25 DEG.C: Not Applicable
VAPOR PRESSURE @ 25 DEG.C: Not Applicable
SOLUBILITY IN WATER: Insoluble
VOLATILES, PERCENT BY VOLUME: Not Applicable
EVAPORATION RATE: Not Applicable
VAPOR DENSITY: Not Applicable
MOLECULAR WEIGHT: Not Applicable/Mixture
ODOR: None
COEFFICIENT OF OIL/WATER DISTRIBUTION: Not Applicable

SECTION 5 PERSONAL PROTECTIVE EQUIPMENT REQUIREMENTS

PERSONAL PROTECTION FOR ROUTINE USE OF PRODUCT:

RESPIRATORY PROTECTION:

Use a NIOSH approved respirator in enclosed firing ranges if airborne dust concentrations ever exceed the PEL or TLV levels for copper or tungsten dust and/or fume.

VENTILATION:

Use local exhaust ventilation in enclosed firing ranges to ensure that airborne concentrations from frangible bullets do not exceed the PEL or TLV.

SKIN AND EYE PROTECTIVE EQUIPMENT:

Use safety glasses.

EQUIPMENT SPECIFICATIONS (WHEN APPLICABLE):

RESPIRATOR TYPE: NIOSH approved respirator with HEPA filters

PROTECTIVE CLOTHING TYPE (This includes: gloves, boots, apron, protective suit): None normally required

SECTION 6 FIRE AND EXPLOSION HAZARD INFORMATION

FLAMMABILITY DATA:

EXPLOSIVE: No

FLAMMABLE: No

COMBUSTIBLE LIQUID: No

PYROPHORIC: No

FLASH POINT: Not Applicable

AUTOIGNITION TEMPERATURE: No Data

FLAMMABLE LIMITS AT NORMAL ATMOSPHERIC TEMPERATURE AND PRESSURE (PERCENT

VOLUME IN AIR): LEL - Not Applicable UEL - Not Applicable

NFPA RATINGS:

Not Established

HMIS RATINGS:

Health: 0

Flammability: 0

Reactivity: 0

EXTINGUISHING MEDIA:

Not Applicable-Choose extinguishing media suitable for surrounding materials.

FIRE FIGHTING TECHNIQUES AND COMMENTS:

Use water to cool containers exposed to fire.

See Section 11 for protective equipment for fire fighting.

NOTE: Dust generated from the impact of frangible bullets with solid targets could conceivably present a fire or explosion hazard under favorable conditions of particle size, dispersion and a strong ignition source. However it is not expected to be a problem in normal circumstances.

SECTION 7 REACTIVITY INFORMATION

CONDITIONS UNDER WHICH THIS PRODUCT MAY BE UNSTABLE:

TEMPERATURES ABOVE: 300 Deg.C (572 Deg.F)

MECHANICAL SHOCK OR IMPACT: No

ELECTRICAL (STATIC) DISCHARGE: No

HAZARDOUS POLYMERIZATION: Will not occur

INCOMPATIBLE MATERIALS: Finely divided tungsten may ignite in contact with a wide range of oxidants, usually on heating

HAZARDOUS DECOMPOSITION PRODUCTS: Carbon monoxide, carbon dioxide, nitrogen oxides and other toxic products of combustion of nylon, and/or release of airborne copper and tungsten powders or their products of combustion

SUMMARY OF REACTIVITY:

EXPLOSIVE:	No
OXIDIZER:	No
PYROPHORIC:	No
ORGANIC PEROXIDE:	No
WATER REACTIVE:	No

SECTION 8 FIRST AID

EYES:

Not an eye irritant.

SKIN:

Not a skin irritant. Washing any substance off the skin with water is a good safety practice.

INGESTION:

Not a likely route of exposure.

INHALATION:

Not a likely route of exposure.

SECTION 9 TOXICOLOGY AND HEALTH INFORMATION

ROUTES OF ABSORPTION

The physical nature of this product makes absorption from any route of exposure unlikely. A small amount of inhalable particles may be created when projectile is fired.

WARNING STATEMENTS AND WARNING PROPERTIES

THIS PRODUCT IS JUDGED TO BE OF LOW TOXICITY AND WILL NOT EXERT A SIGNIFICANT EFFECT TO HEALTH FROM ANY ROUTE OF EXPOSURE.

HUMAN THRESHOLD RESPONSE DATA

ODOR THRESHOLD: No Data

IRRITATION THRESHOLD: No Data

IMMEDIATELY DANGEROUS TO LIFE OR HEALTH: The IDLH concentration has not

been established for this product.

SIGNS, SYMPTOMS, AND EFFECTS OF EXPOSURE:

INHALATION:

No significant adverse effects to health would be expected to occur from inhalation.

Dust generated from the impact of frangible bullets with solid targets will contain tungsten and copper powder coated with nylon. The high density of tungsten ensures that any dust will quickly settle and not remain airborne.

SKIN

There are no known or reported effects from dermal contact with this product.

The molding process generates a thin nylon coating to the bullet which prevents exposure to tungsten and copper powder under normal handling procedures. This nylon coating also reduces the abrasive action of tungsten powder on the skin from any dust generated from the breakup of the bullet on the target.

EYE:

No significant adverse effects to health would be expected to occur from eye contact.

The molding process generates a thin nylon coating to the bullet which prevents exposure to tungsten and copper powder under normal handling procedures. This nylon coating also reduces the abrasive action of tungsten powder on the eyes from any dust generated from the breakup of the bullet on the target.

INGESTION:

There are no known or reported effects from ingestion of this product. The physical nature of this product and its use practically would preclude ingestion as a likely route of exposure to this product.

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE:

Continued inhalation of dust beyond the OSHA permissible exposure limits

(PEL) could aggravate pulmonary (lung) disorders.

INTERACTIONS WITH OTHER CHEMICALS WHICH ENHANCE TOXICITY:

None known or reported.

ANIMAL TOXICOLOGY

ACUTE TOXICITY:

Inhalation LC 50: No Data

Dermal LD 50: No Data

Oral LD 50: No Data

Irritation: Not a skin irritant. Not an eye irritant.

ACUTE TARGET ORGAN TOXICITY:

No organs known to be damaged from exposure to this product.

This product is composed of a solid projectile coated with nylon. It is

judged that the physical nature of the product and its use would preclude the development of any effects from exposure to tungsten or copper.

CHRONIC TARGET ORGAN TOXICITY:

There are no known or reported effects from repeated exposure to this product.

REPRODUCTIVE AND DEVELOPMENTAL TOXICITY:

There are no known or reported effects on reproductive function or fetal

development from exposure to this product.

CARCINOGENICITY:

This product is not known or reported to be carcinogenic by any reference source including IARC, OSHA, NTP, EPA.

MUTAGENICITY:

This product is not known or reported to be mutagenic.

AQUATIC TOXICITY:

No data for product.

SECTION 10 TRANSPORTATION INFORMATION

THIS MATERIAL IS REGULATED AS A DOT HAZARDOUS MATERIAL.

SECTION 11 SPILL AND LEAKAGE PROCEDURES

FOR ALL TRANSPORTATION ACCIDENTS, CALL CHEMTREC AT 800-424-9300.

REPORTABLE QUANTITY: Not Applicable (Per 40 CFR 302.4)

SPILL MITIGATION PROCEDURES:

AIR RELEASE: Not Applicable

WATER RELEASE: This material is heavier than and insoluble in water. Notify all downstream users of possible contamination. Divert water flow around spill if possible and safe to do so.

LAND SPILL: Do not place spill materials back in their original containers. Containerize and label all spill materials properly. Decontaminate all clothing and the spill area using detergent and flush with large amounts of water.

SPILL RESIDUES:

Dispose of per guidelines under Section 12, WASTE DISPOSAL.

PERSONAL PROTECTION FOR EMERGENCY SPILL AND FIRE-FIGHTING SITUATIONS:

In case of fire, use normal fire fighting equipment, including a NIOSH approved self-contained breathing apparatus (SCBA).

SECTION 12 WASTE DISPOSAL

If this product becomes a waste, it DOES NOT meet the criteria of a hazardous waste as defined under 40 CFR 261, in that it does not exhibit the characteristics of hazardous waste of Subpart C, nor is it listed as a hazardous waste under Subpart D.

As a nonhazardous solid waste it should be disposed of in accordance with local, state, and federal regulations by disposal in a secure chemical landfill.

CARE MUST BE TAKEN TO PREVENT ENVIRONMENTAL CONTAMINATION FROM THE USE OF THIS MATERIAL. THE USER OF THIS MATERIAL HAS THE RESPONSIBILITY TO DISPOSE OF UNUSED MATERIAL, RESIDUES AND CONTAINERS IN COMPLIANCE WITH ALL RELEVANT LOCAL, STATE AND FEDERAL LAWS AND REGULATIONS REGARDING TREATMENT, STORAGE AND DISPOSAL FOR HAZARDOUS AND NONHAZARDOUS WASTES.

SECTION 13 ADDITIONAL REGULATORY STATUS INFORMATION

TOXIC SUBSTANCES CONTROL ACT:

This material is exempt under the Article exemption.

SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT TITLE III:

HAZARD CATEGORIES, PER 40 CFR 370.2:

HEALTH:

None

PHYSICAL:

None

EMERGENCY PLANNING AND COMMUNITY RIGHT TO KNOW, PER 40 CFR 355, APP.A:

EXTREMELY HAZARDOUS SUBSTANCE - THRESHOLD PLANNING QUANTITY:

None Established

SUPPLIER NOTIFICATION REQUIREMENTS, PER 40 CFR 372.45:

None Established

SECTION 14 ADDITIONAL INFORMATION

No Additional Information

SECTION 15 MAJOR REFERENCES

References are available upon request.

THIS MATERIAL SAFETY DATA SHEET (MSDS) HAS BEEN PREPARED IN COMPLIANCE WITH THE FEDERAL OSHA HAZARD COMMUNICATION STANDARD, 29 CFR 1910.1200. THE INFORMATION IN THIS MSDS SHOULD BE PROVIDED TO ALL WHO WILL USE, HANDLE, STORE, TRANSPORT, OR OTHERWISE BE EXPOSED TO THIS PRODUCT. THIS INFORMATION HAS BEEN PREPARED FOR THE GUIDANCE OF PLANT ENGINEERING, OPERATIONS AND MANAGEMENT AND FOR PERSONS WORKING WITH OR HANDLING THIS PRODUCT. OLIN BELIEVES THIS INFORMATION TO BE RELIABLE AND UP TO DATE AS OF THE DATE OF PUBLICATION, BUT MAKES NO WARRANTY THAT IT IS. ADDITIONALLY, IF THIS MSDS IS MORE THAN THREE YEARS OLD, YOU

SHOULD CONTACT OUR CORPORATE DIRECTOR: ENVIRONMENT, HEALTH AND SAFETY AT THE PHONE
NUMBER ON THE FRONT PAGE TO MAKE CERTAIN THAT THIS DOCUMENT IS CURRENT.

OLIN CORPORATION
501 Merritt 7
PO Box 4500
Norwalk, CT 06856-4500

Appendix H



MATERIAL SAFETY DATA

FOR ANY EMERGENCY, CALL OCEAN(R) EMERGENCY PHONE(24H):	1-888-289-1911
FOR ALL TRANSPORTATION ACCIDENTS, CALL CHEMTREC@:	1-800-424-9300
FOR ALL MSDS QUESTIONS, CALL CORPORATE DIRECTOR:EH&S:	1-423-336-4007

PRODUCT NAME: CENTERFIRE LEAD FREE PRIMERS

I. PRODUCT AND COMPANY IDENTIFICATION

REVISION DATE: 08-23-1999 SUPERCEDES: 06-16-1999
MSDS NO: 01867-0001 - DPE000188

MANUFACTURER: OLIN CORPORATION 501 Merritt 7 PO Box 4500 Norwalk, CT 06856-4500

SYNONYMS: None
CHEMICAL FAMILY: Mixture
FORMULA: Not Applicable/Mixture
USE DESCRIPTION: Primer
OSHA HAZARD CLASSIFICATION: Explosive (primer mix only); skin and eye irritant

SECTION 2 COMPONENT DATA

PRODUCT COMPOSITION

Product consists of Primer mix (11-15% by weight) enclosed in a Brass cup (85-89% by weight) as follows:

BRASS CUP

CAS or CHEMICAL NAME: Brass alloy 260 - Copper (61-96%);
lead (0.02-0.1%); Zinc (remainder to 100%)

CAS NUMBER: 7440-50-8; 7439-92-1; 7440-66-6

HAZARDOUS PER 29 CFR 1910.1200: Considered non-hazardous so long as used in such a manner as not to produce dust or fumes.

EXPOSURE STANDARDS: (See reference number 5, Section XV; Olin MSDS for Alloy 260.)

PRIMER MIX

CAS or CHEMICAL NAME: Diazodinitro Phenol (Dinol, DDNP)

CAS NUMBER: 4682-03-5

PERCENTAGE RANGE: 2-5% (of product)

HAZARDOUS PER 29 CFR 1910.1200: Yes

EXPOSURE STANDARDS: None Established

CAS or CHEMICAL NAME: Potassium Nitrate

CAS NUMBER: 7757-79-1
PERCENTAGE RANGE: 3-5% (of product)
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS: None Established

CAS or CHEMICAL NAME: Nitrocellulose
CAS NUMBER: 9004-70-0
PERCENTAGE RANGE: 1.5-2.5% (of product)
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS: None Established

CAS or CHEMICAL NAME: Boron Metal
CAS NUMBER: 7440-42-8
PERCENTAGE RANGE: 0.5-1.5% (of product)
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS: as Boron Oxide

	OSHA (PEL)	ACGIH (TLV)
	ppm mg/cubic-meter	ppm mg/cubic-meter
TWA:	15 - total dust 5 - respirable	10
CEILING:	None	None
STEL:	None	None

CAS or CHEMICAL NAME: Nitroglycerine
CAS NUMBER: 55-63-0
PERCENTAGE RANGE: 0.1-0.5% (of product)
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS:

	OSHA (PEL)	ACGIH (TLV)
	ppm mg/cubic-meter	ppm mg/cubic-meter
TWA:	None	0.05 0.46 (skin)
CEILING:	0.2 1 (skin)	None
STEL:	None	None

CAS or CHEMICAL NAME: Tetrazene (1,5-tetrazolyl-4-guanyltetrazene monohydrate)

CAS NUMBER: 109-27-3
PERCENTAGE RANGE: 0.5-1% (of product)
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS: None Established

CAS or CHEMICAL NAME: Nickel
CAS NUMBER: 7440-02-0
PERCENTAGE RANGE: 0.03-0.06% (of product)
HAZARDOUS PER 29 CFR 1910.1200: Not as this concentration
EXPOSURE STANDARDS:

	OSHA (PEL)	ACGIH (TLV)
	ppm mg/cubic-meter	ppm mg/cubic-meter
TWA:	1.0	1.0
CEILING:	None	None
STEL:	None	None

SECTION 3 PRECAUTIONS FOR SAFE HANDLING AND STORAGE

DO NOT TAKE INTERNALLY. AVOID CONTACT WITH SKIN, EYES AND CLOTHING.
UPON CONTACT WITH SKIN OR EYES, WASH OFF WITH WATER.

STORAGE CONDITIONS: STORE IN A COOL, DRY, WELL VENTILATED PLACE.

DO NOT STORE AT TEMPERATURES ABOVE: 65.5 Deg.C (150 Deg.F)
DO NOT SUBJECT TO MECHANICAL SHOCK.

PRODUCT STABILITY AND COMPATIBILITY

SHELF LIFE LIMITATIONS: Indefinite at 50-90 Deg.F and 35% Relative humidity

INCOMPATIBLE MATERIALS FOR PACKAGING: Package only in DOT approved containers.

INCOMPATIBLE MATERIALS FOR STORAGE OR TRANSPORT: Class A & B explosives, strong oxidizers, acids and caustics

SECTION 4 PHYSICAL DATA

APPEARANCE: Brass cup assembly

FREEZING POINT: Not Applicable

BOILING POINT: Not Applicable

DECOMPOSITION TEMPERATURE: 82 Deg.C (180 Deg.F)

SPECIFIC GRAVITY: Not Applicable

BULK DENSITY: No Data

pH @ 25 DEG.C: Not Applicable

VAPOR PRESSURE @ 25 DEG.C: Not Applicable

SOLUBILITY IN WATER: Not Applicable

VOLATILES, PERCENT BY VOLUME: Not Applicable

EVAPORATION RATE: Not Applicable

VAPOR DENSITY: Not Applicable

MOLECULAR WEIGHT: Not Applicable

ODOR: None

COEFFICIENT OF OIL/WATER DISTRIBUTION: Not Applicable

SECTION 5 PERSONAL PROTECTIVE EQUIPMENT REQUIREMENTS

PERSONAL PROTECTION FOR ROUTINE USE OF PRODUCT:

RESPIRATORY PROTECTION:

Respiratory protection not normally needed. If significant dusting occurs, wear a NIOSH approved respirator.

VENTILATION:

Local exhaust ventilation is recommended if significant dusting occurs. Otherwise, use general exhaust ventilation. Use explosion-proof ventilation when handling this product.

SKIN AND EYE PROTECTIVE EQUIPMENT:

Use chemical goggles and impermeable gloves..

EQUIPMENT SPECIFICATIONS (WHEN APPLICABLE):

RESPIRATOR TYPE: NIOSH approved respirator equipped with HEPA filter cartridge.

PROTECTIVE CLOTHING TYPE (This includes: gloves, boots, apron, protective suit): Impervious

SECTION 6 FIRE AND EXPLOSION HAZARD INFORMATION

FLAMMABILITY DATA:

EXPLOSIVE: Yes (primer mix only)

FLAMMABLE: Not Applicable
COMBUSTIBLE: Not Applicable
PYROPHORIC: No
FLASH POINT: Not Applicable
AUTOIGNITION TEMPERATURE: No Data
FLAMMABLE LIMITS AT NORMAL ATMOSPHERIC TEMPERATURE AND PRESSURE
(PERCENT
VOLUME IN AIR): LEL - Not Applicable UEL - Not Applicable

NFPA RATINGS:
Not Established

HMIS RATINGS:
Health: 2
Flammability: 0
Reactivity: 3

EXTINGUISHING MEDIA:

Try to prevent fire from reaching cargo. If fire reaches cargo, evacuate for a distance of at least 50 feet. Do not fight, flood with water. If no water is available, use dry chemical or carbon dioxide.

FIRE FIGHTING TECHNIQUES AND COMMENTS:

Use water to cool containers exposed to fire.
See Section 11 for protective equipment for fire fighting.

SECTION 7 REACTIVITY INFORMATION

CONDITIONS UNDER WHICH THIS PRODUCT MAY BE UNSTABLE:

TEMPERATURES ABOVE: 82 Deg.C (180 Deg.F)

MECHANICAL SHOCK OR IMPACT: Yes

ELECTRICAL (STATIC) DISCHARGE: yes

OTHER: Friction

HAZARDOUS POLYMERIZATION: Will not occur

INCOMPATIBLE MATERIALS: Acids, caustics, strong oxidizers

HAZARDOUS DECOMPOSITION PRODUCTS: Nitrogen oxides, carbon monoxide

SUMMARY OF REACTIVITY:

EXPLOSIVE: Yes (primer mix only)
OXIDIZER: No
PYROPHORIC: No
ORGANIC PEROXIDE: No
WATER REACTIVE: No

SECTION 8 FIRST AID

EYES:

Immediately flush with large amounts of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. If eye irritation develops, call a physician.

SKIN: May cause minor skin irritation. Cleanse skin by washing.

INGESTION: Not a likely route of exposure.

INHALATION: Not a likely route of exposure.

SECTION 9 TOXICOLOGY AND HEALTH INFORMATION

ROUTES OF ABSORPTION

Eye and skin contact, inhalation, ingestion.

WARNING STATEMENTS AND WARNING PROPERTIES

DO NOT TAKE INTERNALLY. MAY BE HARMFUL IF SWALLOWED. CONTACT WITH PRIMER MAY CAUSE IRRITATION TO SKIN, EYES AND MUCOUS MEMBRANES.

HUMAN THRESHOLD RESPONSE DATA

ODOR THRESHOLD: No data

IRRITATION THRESHOLD: No data

IMMEDIATELY DANGEROUS TO LIFE OR HEALTH: The IDLH concentration has not been established for this product.

SIGNS, SYMPTOMS, AND EFFECTS OF EXPOSURE:

INHALATION

ACUTE: The product is a solid pellet. It is judged that the physical nature would preclude inhalation.

CHRONIC: The product is a solid pellet. It is judged that the physical nature would preclude inhalation.

SKIN

ACUTE: Dermal exposure to the primer may cause irritation, which would subside rapidly upon removal of material without permanent damage. Dilation of blood vessels with drop in blood pressure and headache, cyanosis, and mental confusion may result from the nitroglycerin. The headache may be severe and can remain for a few hours to several days. It typically starts at the forehead preceded by a sensation of warmth and fullness and abdominal pain may also occur.

CHRONIC: No additional effects are known or have been reported except for those described for acute exposure.

EYE

If the primer comes into contact with the eyes, irritation may occur with inflammation of the conjunctiva. Any effect would not result in permanent impairment of vision.

INGESTION

ACUTE: Ingestion of the primer may cause irritation to the gastrointestinal tract. Ingestion of the primer may also cause GI discomfort with any or all of the following symptoms: nausea, vomiting, lethargy or diarrhea. Additional effects would be similar to those described for acute skin exposure.

CHRONIC: No additional effects are known or have been reported except for those described for acute skin exposure.

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE:

None known or reported.

INTERACTIONS WITH OTHER CHEMICALS WHICH ENHANCE TOXICITY:

None known or reported.

ANIMAL TOXICOLOGY

ACUTE TOXICITY:

Inhalation LC 50: No data
Dermal LD 50: No data
Oral LD 50: No data

Irritation: Irritant to skin, eyes, mucous membranes and respiratory tract

ACUTE TARGET ORGAN TOXICITY:

Contact with the primer would be expected to cause irritation to skin, eyes and mucous membranes. Ingestion of the primer may cause irritation and gastrointestinal discomfort with any or all of the following symptoms: nausea, vomiting, lethargy, or diarrhea. Nitroglycerin will produce dilation of blood vessels and drop in blood pressure, which may affect the heart. It has also been shown to cause methemoglobinemia (cyanosis).

CHRONIC TARGET ORGAN TOXICITY:

No organs known or reported to be damaged from chronic exposure to this product.

REPRODUCTIVE AND DEVELOPMENTAL TOXICITY:

There are no known or reported effects on reproductive function or fetal development.

CARCINOGENICITY: This product is not known or reported to be carcinogenic by any reference source including IARC, OSHA, NTP, or EPA. Lead is classified as a carcinogen by IARC. Lead and inorganic lead compounds are also classified as carcinogens by EPA. Based on the physical nature of the product and its use, it is judged that the risk of cancer is not significant from exposure to the product.

MUTAGENICITY: This product is not known or reported to be mutagenic.

AQUATIC TOXICITY: No data for product

SECTION 10 TRANSPORTATION INFORMATION

THIS MATERIAL IS REGULATED AS A DOT HAZARDOUS MATERIAL.

DOT DESCRIPTION FROM THE HAZARDOUS MATERIALS TABLE 49 CFR 172.101:
LAND (U.S. DOT): PRIMERS, CAP TYPE, 1.4S, UN0044, PG II

WATER (IMO): SAME AS LAND

AIR (IATA/ICAO): SAME AS LAND

HAZARD LABEL/PLACARD: None for land*

REPORTABLE QUANTITY: 100 lbs. (45.5 Kg.) - Per 49 CFR 172.101, Appendix)

Reportable quantity applicable only if primers become hazardous waste

EMERGENCY GUIDE NO: 114

SPECIAL COMMENTS: * 1.4S label for air/water; 1.4S Placard if 100 lbs. or more are loaded on a vehicle for Air Freight Shipment or in an ocean container. Package marks: PRIMERS, CAP TYPE UN0044 and either Product Symbol or EX-9403188.

SECTION 11 SPILL AND LEAKAGE PROCEDURES

FOR ALL TRANSPORTATION ACCIDENTS, CALL CHEMTREC AT 800-424-9300.

REPORTABLE QUANTITY: This product is subject to a Reportable Quantity with respect to nitroglycerin. RQs are subject to change and reference should be made to 40 CFR 302.4 for the current requirements.

SPILL MITIGATION PROCEDURES:

Evacuation procedures must be placed into effect. Hazardous concentrations in air may be found in local spill area. This product may represent an explosion hazard. Remove all sources of ignition. Stop source of spill as soon as possible and notify appropriate personnel.

AIR RELEASE: Not applicable

WATER RELEASE: This material is heavier than, and not soluble in water.

LAND SPILL: A spill of this material will normally not require emergency team capabilities. If however, a large spill occurs, contact OCEAN at 1-800-OLIN-911. At all times, use non-sparking tools, and do not subject material to mechanical shock. Do not place spill materials back in their original containers. Containerize and label all spill materials properly. Decontaminate all clothing and the spill area using detergent and flush with large amounts of water.

SPILL RESIDUES:

Dispose of per guidelines under Section 12, WASTE DISPOSAL.

PERSONAL PROTECTION FOR EMERGENCY SPILL AND FIRE-FIGHTING SITUATIONS: Response to this material requires the use of a full encapsulated suit and self-contained breathing apparatus (SCBA). A hazardous physical characteristic of this product is: Explosive

SECTION 12 WASTE DISPOSAL

If this product becomes a waste, it meets the criteria of a hazardous waste as defined under 40 CFR 261 and would have the following EPA hazardous waste number: D003.

If this product becomes a waste, it will be a hazardous waste, which is subject to the Land Disposal Restrictions under 40 CFR 268 and must be managed accordingly.

Other: Send for Metal Reclamation

CARE MUST BE TAKEN TO PREVENT ENVIRONMENTAL CONTAMINATION FROM THE USE OF THIS MATERIAL. THE USER OF THIS MATERIAL HAS THE RESPONSIBILITY TO DISPOSE OF UNUSED MATERIAL, RESIDUES AND CONTAINERS IN COMPLIANCE WITH ALL RELEVANT LOCAL, STATE AND FEDERAL LAWS AND REGULATIONS REGARDING TREATMENT, STORAGE AND DISPOSAL FOR HAZARDOUS AND NONHAZARDOUS WASTES.

SECTION 13 ADDITIONAL REGULATORY STATUS INFORMATION

TOXIC SUBSTANCES CONTROL ACT:

The components of this product are listed on the Toxic Substance Control Act inventory.

CALIFORNIA SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986 -
PROPOSITION 65:

"WARNING: This product contains detectable amounts of a chemical(s) known to the State of California to cause cancer and/or birth

defects or other reproductive harm."

SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT TITLE III:
HAZARD CATEGORIES, PER 40 CFR 370.2:

HEALTH:

Immediate (Acute)

PHYSICAL:

Sudden release of pressure

EMERGENCY PLANNING AND COMMUNITY RIGHT TO KNOW, PER 40 CFR 355, APP.A:
EXTREMELY HAZARDOUS SUBSTANCE - THRESHOLD PLANNING QUANTITY:
None Established

SUPPLIER NOTIFICATION REQUIREMENTS, PER 40 CFR 372.45:
Not Applicable - considered to be an article

SECTION 14 ADDITIONAL INFORMATION

MSDS REVISION STATUS: Minor revision to Exposure Standards; HMIS
Ratings
revised

SECTION 15 MAJOR REFERENCES

1. Sittig, Marshall, Handbook of Toxic and Hazardous Chemicals and Carcinogens, 2nd Ed., Noyes Publications, Park Ridge, NJ, 1985.
 2. NIOSH Criteria for a Recommended Standard . . . Occupational Exposure to Nitroglycerin and Ethylene Glycol Dinitrate.
 3. Rose, et al., Analysis of Recent Industry Medical Studies. Prepared for The Explosives Industry Ad Hoc Committee Washington, D.C.: U.S. Government Printing Office, June 1978. Washington, D.C., 1981.,
 4. Lee, Cheng-Chun, et al., Mammalian Toxicity of Munition Compounds: Phase I. Acute Oral Toxicity, Primary Skin and Eye Irritation, Dermal Sensitization, and Disposition and Metabolism. NTIS Report (ADB011150), National Technical Information Services, Springfield, VA. Report No. 1, July 22, 1975.
 5. Olin MSDS for Alloy 260, File BPE00077.0011, Product Code BPE020260
- Other References are available upon request.

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OLIN CORPORATION
501 Merritt 7
PO Box 4500
Norwalk, CT 06856-4500

Appendix I



MATERIAL SAFETY DATA

FOR ANY EMERGENCY, CALL OCEAN(R) EMERGENCY PHONE(24H):	1-888-289-1911
FOR ALL TRANSPORTATION ACCIDENTS, CALL CHEMTREC®:	1-800-424-9300
FOR ALL MSDS QUESTIONS, CALL CORPORATE DIRECTOR:EH&S:	1-423-336-4007

PRODUCT NAME: CENTERFIRE PISTOL LOADED ROUND

I. PRODUCT AND COMPANY IDENTIFICATION

REVISION DATE: 08-19-1999
MSDS NO: 00825-0002 - DPE000094

SUPERCEDES: 06-15-1999

MANUFACTURER: OLIN CORPORATION 501 Merritt 7 PO Box 4500 Norwalk, CT 06856-4500

SYNONYMS: Super-X Centerfire Pistol/Revolver: 25 Automatic (6.35mm) Expanding Point and Full Metal Case; 30 Luger (7.65mm) Full Metal Case; 30 Carbine Hollow Soft Point and Full Metal Case; 32 Smith & Wesson Lead Round Nose and Long Lead Round Nose; 32 Short and Long Colt Lead Round Nose; 32 Automatic Silvertip Hollow Point and Full Metal Case; 38 Smith & Wesson Lead Round Nose, 380 Automatic Silvertip Hollow Point and Full Metal Case; 38 Special Silvertip Hollow Point, Lead Round Nose, Lead Semi-Wad Cutter, Metal Point, Silvertip Hollow Point + P, Jacketed Hollow Point + P, Lead Hollow Point + P, Lead Semi-Wad Cutter + P, Match Lead Mid-Range Match; 9mm Luger(Parabellum): Full Metal Jacket Encapsulated, Full Metal Case, Silvertip Hollow Point; 38 Super Automatic Silvertip Hollow point + P, Full Metal Case + P; 357 Magnum Jacketed Hollow Point, Silvertip Hollow Point, Lead Semi-Wad Cutter, Jacketed Soft Point; 10mm Automatic Silvertip Hollow Point; 41 Remington Magnum Silvertip Hollow Point, Lead Semi-Wad Cutter, Jacketed Soft Point, Jacketed Hollow Point; 44 Smith & Wesson Special Silvertip Hollow Point, Hollow Soft Point; 44 Remington Magnum Silvertip Hollow Point, Hollow Soft Point, Lead Semi-Wad Cutter.(Med. Vel. & Gas Check); 45 Automatic Silvertip Hollow Point + P, Full Metal Case, Super-Match Full Metal Case Semi-Wad Cutter; 45 Colt Silvertip Hollow Point, Lead Round Nose; 45 Winchester Magnum: Jacketed Soft Point, Full Metal Case; Black Talon; 40 Smith and Wesson: Silvertip Hollow Point, Full Metal Jacket Truncated Cone, Full Metal Jacket Encapsulated, Jacket Hollow Point, Full Metal Jacket, Supreme 357 Magnum 180 gr. Partition Bullet, Supreme 44 Magnum 250 gr. Partition Bullet; Ranger Talon, 40 Cal. 180 gr. JHP; Ranger Talon, 45 Auto, 230 gr. JHP; Ranger Talon, 9mm, 147 gr. JHP

CHEMICAL FAMILY: Mixture
FORMULA: Not Applicable/Mixture

USE DESCRIPTION: Loaded round
OSHA HAZARD CLASSIFICATION: Explosive

SECTION 2 COMPONENT DATA

PRODUCT COMPOSITION

Consists of the following four components:

NUMBER	COMPONENT	PERCENT	PRODUCT	PRODUCT CODE
A) Projectile DPE.000022		30-70%	Centerfire Bullets	
B) Shell Case BPE.020000		30-60%	Brass 2XXX Series	
C) Propellant DPE.090000		5-10%	Smokeless Powder	
D) Centerfire Primer DPE.020000		1-4%	Centerfire Primers	

Additional information may be obtained from Olin by requesting the MSDS for any component of interest and quoting the relevant product code number.

All percent compositions specified below are based on the entire product.

A) Projectile

CAS or CHEMICAL NAME: Lead

CAS NUMBER: 7439-92-1

PERCENTAGE RANGE: 30-70%

HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)

EXPOSURE STANDARDS: See 29 CFR 1910.1025

	OSHA (PEL)	ACGIH (TLV)		
	ppm	mg/cubic-meter	ppm	mg/cubic-meter
TWA:	0.05		0.15	
CEILING:	None		None	
STEL:	None		None	

CAS or CHEMICAL NAME: Iron

CAS NUMBER: 7439-89-6

PERCENTAGE RANGE: 0-38%

HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)

EXPOSURE STANDARDS: As iron oxide fume

	OSHA (PEL)	ACGIH (TLV)		
	ppm	mg/cubic-meter	ppm	mg/cubic-meter
TWA:	10		5	
CEILING:	None		None	
STEL:	None		None	

CAS or CHEMICAL NAME: Copper

CAS NUMBER: 7440-50-8

PERCENTAGE RANGE: 0-25%

HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)
EXPOSURE STANDARDS: As copper dust

	OSHA(PEL)	ACGIH(TLV)
	ppm mg/cubic-meter	ppm mg/cubic-meter
TWA:	1	1
CEILING:	None	None
STEL:	None	None

CAS or CHEMICAL NAME: Zinc
CAS NUMBER: 7440-66-6
PERCENTAGE RANGE: 0-6%
HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)
EXPOSURE STANDARDS: As zinc oxide

	OSHA(PEL)	ACGIH(TLV)
	ppm mg/cubic-meter	ppm mg/cubic-meter
TWA:	5 (respirable) 10 (total)	10
CEILING:	None	None
STEL:	None	None

CAS or CHEMICAL NAME: Aluminum
CAS NUMBER: 7429-90-5
PERCENTAGE RANGE: 0-6%
HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)
EXPOSURE STANDARDS:

	OSHA(PEL)	ACGIH(TLV)
	ppm mg/cubic-meter	ppm mg/cubic-meter
TWA:	5 (respirable) 15 (total)	10
CEILING:	None	None
STEL:	None	None

CAS or CHEMICAL NAME: Antimony
CAS NUMBER: 7440-36-0
PERCENTAGE RANGE: .2-2%
HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)
EXPOSURE STANDARDS:

	OSHA(PEL)	ACGIH(TLV)
	ppm mg/cubic-meter	ppm mg/cubic-meter
TWA:	0.5	0.5
CEILING:	None	None
STEL:	None	None

B) Shellcase

CAS or CHEMICAL NAME: Copper (see above)
CAS NUMBER: 7440-50-8
PERCENTAGE RANGE: 30-45%

CAS or CHEMICAL NAME: Zinc (see above)
CAS NUMBER: 7440-66-6

PERCENTAGE RANGE: 10-20%

C) Propellant

CAS or CHEMICAL NAME: Nitrocellulose
CAS NUMBER: 9004-70-0
PERCENTAGE RANGE: 5-10%
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS: None Established

CAS or CHEMICAL NAME: Nitroglycerin
CAS NUMBER: 55-63-0
PERCENTAGE RANGE: .5-2%
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS:

	OSHA(PEL)	ACGIH(TLV)
	ppm	mg/cubic-meter
TWA:	0.1 (skin)	0.05 (skin)
CEILING:	None	None
STEL:	None	None

CAS or CHEMICAL NAME: Dibutyl phthalate
CAS NUMBER: 84-74-2
PERCENTAGE RANGE: .5-2%
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS:

	OSHA(PEL)	ACGIH(TLV)
	ppm	mg/cubic-meter
TWA:	5	5
CEILING:	None	None
STEL:	None	None

D) Centerfire Primer

CAS or CHEMICAL NAME: Copper (See above)
CAS NUMBER: 7440-50-8
PERCENTAGE RANGE: .5-3%

CAS or CHEMICAL NAME: Zinc (See above)
CAS NUMBER: 7440-66-6
PERCENTAGE RANGE: .1-1%

CAS or CHEMICAL NAME: Lead styphnate
CAS NUMBER: 15245-44-0
PERCENTAGE RANGE: .1-1%
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS: as lead (See 29 CFR 1910.1025)

	OSHA(PEL)	ACGIH(TLV)
	ppm	mg/cubic-meter
TWA:	0.05	0.15
CEILING:	None	None
STEL:	None	None

CAS or CHEMICAL NAME: Barium nitrate
CAS NUMBER: 10022-31-8
PERCENTAGE RANGE: .1-1%
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS:

	OSHA (PEL)	ACGIH (TLV)		
	ppm	mg/cubic-meter	ppm	mg/cubic-meter
TWA:		0.5		0.5
CEILING:	None		None	
STEL:	None		None	

SECTION 3 PRECAUTIONS FOR SAFE HANDLING AND STORAGE

DO NOT TAKE INTERNALLY. AVOID CONTACT WITH SKIN, EYES AND CLOTHING.
UPON CONTACT WITH SKIN OR EYES, WASH OFF WITH WATER.

STORAGE CONDITIONS:

STORE IN A COOL, DRY, WELL VENTILATED PLACE, AWAY FROM ALL SOURCES OF IGNITION

DO NOT STORE AT TEMPERATURES ABOVE: Not Applicable

DO NOT SUBJECT TO MECHANICAL SHOCK.

PRODUCT STABILITY AND COMPATIBILITY

SHELF LIFE LIMITATIONS: 25-30 Years

INCOMPATIBLE MATERIALS FOR STORAGE OR TRANSPORT: Acids

SECTION 4 PHYSICAL DATA

APPEARANCE: Finished cartridge

FREEZING POINT: Not Applicable

BOILING POINT: Not Applicable

DECOMPOSITION TEMPERATURE: Not Applicable

SPECIFIC GRAVITY: Not Applicable

BULK DENSITY: Not Applicable

pH @ 25 DEG.C: Not Applicable

VAPOR PRESSURE @ 25 DEG.C: Not Applicable

SOLUBILITY IN WATER: Not Applicable

VOLATILES, PERCENT BY VOLUME: Not Applicable

EVAPORATION RATE: Not Applicable

VAPOR DENSITY: Not Applicable

MOLECULAR WEIGHT: Not Applicable

ODOR: None

COEFFICIENT OF OIL/WATER DISTRIBUTION: Not Applicable

SECTION 5 PERSONAL PROTECTIVE EQUIPMENT REQUIREMENTS

PERSONAL PROTECTION FOR ROUTINE USE OF PRODUCT:

RESPIRATORY PROTECTION: Not normally required

VENTILATION: None beyond normal ventilation

SKIN AND EYE PROTECTIVE EQUIPMENT: Use safety glasses.

EQUIPMENT SPECIFICATIONS (WHEN APPLICABLE):

RESPIRATOR TYPE: Not normally required
PROTECTIVE CLOTHING TYPE (This includes: gloves, boots, apron, protective suit): Not normally required

SECTION 6 FIRE AND EXPLOSION HAZARD INFORMATION

FLAMMABILITY DATA:

EXPLOSIVE: Yes
FLAMMABLE: Not Applicable
COMBUSTIBLE: Not Applicable
PYROPHORIC: No
FLASH POINT: Not Applicable
AUTOIGNITION TEMPERATURE: No Data
FLAMMABLE LIMITS AT NORMAL ATMOSPHERIC TEMPERATURE AND PRESSURE
(PERCENT VOLUME IN AIR): LEL - Not Applicable UEL - Not Applicable

NFPA RATINGS: Not Established

HMIS RATINGS:

Health: 0
Flammability: 2
Reactivity: 4

EXTINGUISHING MEDIA:

Water spray

Other: Do not fight fire, if fire reaches cargo, flood with water from unmanned hoses.

FIRE FIGHTING TECHNIQUES AND COMMENTS:

See Section 11 for protective equipment for fire fighting.
Evacuate all persons including emergency personnel from the area for 1500 feet (1/2 mile) in all directions, if fire reaches cargo.

SECTION 7 REACTIVITY INFORMATION

CONDITIONS UNDER WHICH THIS PRODUCT MAY BE UNSTABLE:

TEMPERATURES ABOVE: No Data
MECHANICAL SHOCK OR IMPACT: Yes - based on primer
ELECTRICAL (STATIC) DISCHARGE: Yes - based on primer
OTHER: CARTRIDGE MAY DETONATE IF CASE IS PUNCTURED OR SEVERELY DAMAGED
HAZARDOUS POLYMERIZATION: Will not occur
INCOMPATIBLE MATERIALS: Acids
HAZARDOUS DECOMPOSITION PRODUCTS: Nitrogen oxides, Carbon monoxide, carbon dioxide, lead oxides, lead dust /fume
OTHER CONDITIONS TO AVOID: CARTRIDGES PLACED IN A HIGH RADIO FREQUENCY ENERGY FIELD (RADAR STATIONS)

SUMMARY OF REACTIVITY:

EXPLOSIVE: Yes
OXIDIZER: No
PYROPHORIC: No
ORGANIC PEROXIDE: No
WATER REACTIVE: No

SECTION 8 FIRST AID

EYES: Not a likely route of exposure.

SKIN: Not a likely route of exposure.

INGESTION: Not a likely route of exposure.

INHALATION: Not a likely route of exposure.

SECTION 9 TOXICOLOGY AND HEALTH INFORMATION

ROUTES OF ABSORPTION

The physical nature of this product makes absorption from any route unlikely. A small amount of inhalable particles may be created when projectile is fired.

WARNING STATEMENTS AND WARNING PROPERTIES

PARTICLES FROM FIRING MAY BE HARMFUL IF INHALED.

HUMAN THRESHOLD RESPONSE DATA

ODOR THRESHOLD: No available data

IRRITATION THRESHOLD: No available data

IMMEDIATELY DANGEROUS TO LIFE OR HEALTH: The IDLH concentration has not been established.

SIGNS, SYMPTOMS, AND EFFECTS OF EXPOSURE

INHALATION

ACUTE: Inhalation of lead dust or metal fume may cause irritation to nose, throat, upper respiratory tract and lung. The irritant effects may lead to bronchitis, headache, a fall in blood pressure, weakness, convulsions and collapse may occur. Severe poisoning may impair vision by damaging the optic nerve. The product is composed of a solid projectile. It is judged that the physical nature of the product, and its use would preclude inhalation of a sufficient amount of lead and the development of these symptoms.

CHRONIC: Chronic inhalation of lead dust or metal fume may cause damage to central and peripheral nerves, blood, kidneys and the fetus. Male reproductive function may be impaired. Damage to nerves can result in reduction in motor nerve and muscle function. Anemia may result due to interference by lead of hemoglobin synthesis. Lead has been identified as an animal carcinogen; it may produce cancer in humans. Chronic exposure may lead to lead poisoning, known as "Plumbism", causing gingival lead line and an accumulation in body tissues. The product is composed of a solid projectile. It is judged that the of the product, and its use would preclude inhalation of a sufficient amount of lead and the development of these symptoms. physical nature

SKIN

ACUTE: Lead can be absorbed through the skin to produce effects similar to those listed for acute inhalation exposure.

CHRONIC: Lead can be absorbed through the skin to produce effects similar to those listed under chronic inhalation exposure. The product

is composed of a solid projectile. It is judged that the physical nature of the product, and its use would preclude skin absorption of a sufficient amount of lead and the development of these acute and/or chronic symptoms.

EYE

Lead dust and fume can irritate the eyes with conjunctival redness and discharge. It is judged that this effect would not occur because of the physical nature of the product and its use.

INGESTION

ACUTE: The effects of lead ingestion would be similar to those listed under acute inhalation exposure in addition to gastrointestinal tract irritation.

CHRONIC: The effects of lead ingestion would be similar to those listed under chronic inhalation exposure. The product is composed of a solid projectile. It is judged that the physical nature of the product, and its use would preclude ingestion and the development of these acute and/or chronic symptoms.

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE

Exposure to lead can aggravate anemia, cardiovascular and respiratory disease. There are no medical conditions known to be aggravated by exposure to this product, due to its physical nature and use.

INTERACTIONS WITH OTHER CHEMICALS WHICH ENHANCE TOXICITY

There are no chemicals known to enhance the toxicity of the product.

ANIMAL TOXICOLOGY

ACUTE TOXICITY:

- Inhalation LC 50: No available data
- Dermal LD 50: No available data
- Oral LD 50: No available data
- Irritation: Not a skin or eye irritant.

ACUTE TARGET ORGAN TOXICITY: Lead dust and fume can cause damage to central nervous system, blood, lungs and eyes.

CHRONIC TARGET ORGAN TOXICITY: Inhalation of lead can cause damage to the blood, central and peripheral nervous systems, and kidney. Lead inhibits the production of hemoglobin, the material in the blood, which carries oxygen. Anemia may result. Lead also causes damage to peripheral nerves resulting in a decrease in motor nerve and muscle function. The product is composed of a solid projectile. It is judged that the physical nature of the product and its use would preclude the development of these effects. Inhalation of iron dust or fumes has been shown to cause a benign pneumoconiosis known as siderosis. This condition is characterized by deposition of iron in the lungs without subsequent fibrotic changes or impairment of lung function. The physical nature of the product, the low percentage of iron in the product, and its use would preclude the development of siderosis. Inhalation of aluminum dust or fume has produced lung fibrosis in laboratory animals. It is judged that the physical nature of the product, the low percentage of aluminum in the product, and its use would preclude the development of lung fibrosis.

REPRODUCTIVE AND DEVELOPMENTAL TOXICITY:

Lead has been shown to affect fetal development and reduce male reproductive function. Lead crosses the placenta and may affect the

fetus causing birth defects, mental retardation, behavioral disorders, and death during the first year of childhood. The product is composed of a solid projectile. It is judged that the physical nature and use of the product would preclude the development of these effects.

CARCINOGENICITY:

This product is not known or reported to be carcinogenic by any reference source including IARC, OSHA, NTP, or EPA. Lead is classified as a carcinogen by IARC. Based on the physical nature of the product and its use, it is judged that the risk of cancer is not significant from exposure to the product:

MUTAGENICITY:

This product is not known or reported to be mutagenic.

AQUATIC TOXICITY:

The LC 50 of lead (48 hrs.) to bluegill (*Lepomis macrochirus*) is reported to be 2-5 mg/l.

SECTION 10 TRANSPORTATION INFORMATION

THIS MATERIAL IS REGULATED AS A DOT HAZARDOUS MATERIAL.

DOT DESCRIPTION FROM THE HAZARDOUS MATERIALS TABLE 49 CFR 172.101:

LAND (U.S. DOT): CARTRIDGES, SMALL ARMS (OTHER THAN BLANKS), 1.4S,
UN0012, PG II

WATER (IMO): SAME AS ABOVE

AIR (IATA/ICAO): SAME AS ABOVE

HAZARD LABEL/PLACARD: NONE REQUIRED

REPORTABLE QUANTITY: NOT APPLICABLE (Per 49 CFR 172.101, Appendix)

EMERGENCY GUIDE NO: 114

SPECIAL COMMENTS: May be reclassified domestically as an ORM-D if appropriately packaged per 49 CFR 173.203.

SECTION 11 SPILL AND LEAKAGE PROCEDURES

FOR ALL TRANSPORTATION ACCIDENTS, CALL CHEMTREC AT 800-424-9300.

REPORTABLE QUANTITY: (Per 40 CFR 302.4) as nitroglycerine 10#, dibutyl phthalate 10#

SPILL MITIGATION PROCEDURES:

This product does represent an explosion hazard when involved in a fire or exposed to heat, friction, shock, etc. Remove all sources of ignition.

AIR RELEASE: Not Applicable

WATER RELEASE: Not Applicable

LAND SPILL: Shut off ignition sources, no flares, smoking or flames in hazard area. Place in proper DOT container, for later disposition.

SPILL RESIDUES:

Dispose of per guidelines under Section 12, WASTE DISPOSAL.

PERSONAL PROTECTION FOR EMERGENCY SPILL AND FIRE-FIGHTING SITUATIONS:

- No extra protection required beyond that listed in Section 5 (In case of fire, use normal fire fighting equipment).
- Protection concerns must also address the potential of the physical characteristic of this product as explosive.

SECTION 12 WASTE DISPOSAL

If this product becomes a waste, it meets the criteria of a hazardous waste as defined under 40 CFR 261 and would have the following EPA hazardous waste number: D003.

If this product becomes a waste, it will be a hazardous waste, which is subject to the Land Disposal Restrictions under 40 CFR 268 and must be managed accordingly.

Other: Deactivation.

CARE MUST BE TAKEN TO PREVENT ENVIRONMENTAL CONTAMINATION FROM THE USE OF THIS MATERIAL. THE USER OF THIS MATERIAL HAS THE RESPONSIBILITY TO DISPOSE OF UNUSED MATERIAL, RESIDUES AND CONTAINERS IN COMPLIANCE WITH ALL RELEVANT LOCAL, STATE AND FEDERAL LAWS AND REGULATIONS REGARDING TREATMENT, STORAGE AND DISPOSAL FOR HAZARDOUS AND NONHAZARDOUS WASTES.

SECTION 13 ADDITIONAL REGULATORY STATUS INFORMATION

TOXIC SUBSTANCES CONTROL ACT:

The components of this product are listed on the Toxic Substance Control Act inventory.

CALIFORNIA SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986 - PROPOSITION 65:

"WARNING: This product contains detectable amounts of a chemical(s) known to the State of California to cause cancer and/or birth defects or other reproductive harm."

SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT TITLE III:

HAZARD CATEGORIES, PER 40 CFR 370.2:

HEALTH: None

PHYSICAL: Sudden release of pressure

EMERGENCY PLANNING AND COMMUNITY RIGHT TO KNOW, PER 40 CFR 355, APP.A:

EXTREMELY HAZARDOUS SUBSTANCE - THRESHOLD PLANNING QUANTITY:

None Established

SUPPLIER NOTIFICATION REQUIREMENTS, PER 40 CFR 372.45:

None Established

SECTION 14 ADDITIONAL INFORMATION

MSDS REVISION STATUS: Synonyms Added

SECTION 15 MAJOR REFERENCES

1. Friberg, L., G.F. Nordberg, and V.B. Vouk, eds., Handbook on the Toxicology of Metals, Vol. II, Elsevier, New York, 1986.

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OLIN CORPORATION

501 Merritt 7
PO Box 4500
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Appendix J



MATERIAL SAFETY DATA

FOR ANY EMERGENCY, CALL OCEAN(R) EMERGENCY PHONE(24H):	1-888-289-1911
FOR ALL TRANSPORTATION ACCIDENTS, CALL CHEMTREC®:	1-800-424-9300
FOR ALL MSDS QUESTIONS, CALL CORPORATE DIRECTOR:EH&S:	1-423-336-4007

PRODUCT NAME: CENTERFIRE RIFLE LOADED ROUND

I. PRODUCT AND COMPANY IDENTIFICATION

REVISION DATE: 08-19-1999 SUPERCEDES: 06-15-1999
MSDS NO: 00796-0001 - DPE000096

MANUFACTURER: OLIN CORPORATION 501 Merritt 7 PO Box 4500 Norwalk, CT 06856-4500

SYNONYMS: Super-X Centerfire Rifle:

218 Bee, 22 Hornet, 22-250 Remington, 222 Remington, 223 Remington, 225 Winchester, 243 Winchester, 6mm Remington, 25-06 Remington 25-20 Winchester, 25-35 Winchester, 250 Savage, 257 Roberts + P, 264 Winchester Mag., 270 Winchester, 284 Winchester, 7mm Mauser (7 x 57), 7mm Remington Mag., 30 Carbine, 30-30 Winchester, 30-06 Springfield, 30-40 Krag, 300 Winchester Mag., 300 H & H Magnum, 300 Savage, 303 Savage, 303 British, 307 Winchester, 308 Winchester, 32 Win. Special, 32-20 Winchester, 8mm Mauser (8 x57), 338 Winchester Mag., 35 Remington, 356 Winchester, 357 Magnum, 358 Winchester, 375 Winchester, 375 H & H Magnum, 38-40 Winchester, 38-55 Winchester, 44 Remington Magnum, 44-40 Winchester, 45-70 Government, 458 Winchester Mag, 280 Remington, Supreme 243 Winchester, Supreme 22-250 Remington, Supreme 270 Winchester, Supreme 280 Remington, Supreme 7mm Remington Magnum, Supreme 30-30 Winchester, Supreme 308 Winchester, Supreme 30-06 Springfield, Supreme 300 Winchester Magnum, 223 Remington 55 gr. Pointed Soft Point Varminator, 22-250 Remington, 55 gr. Pointed Soft Point Varminator, 22 Hornet, 46 gr. Hollowpoint, Varminator, 243 Winchester, 100 gr. Power Point, Varminator, 222 Remington, 50 gr. Pointed Soft Point, Varminator, 220 Swift, 55 gr. Pointed Soft Point Varminator, 25-06 Remington, 90 gr. Positive Expanding Point, Varminator, 454 Casull, 260 gr. Jacketed Flat Point, 454 Casull, 300 gr. Jacketed Flat Point, 30-06 Springfield, 150 gr. Fail Safe, 280 Remington, 140 gr. Fail Safe, 7MM Remington Magnum, 140 gr. Fail Safe, 220 Swift, 40 gr. Ballistic Silvertip, 22-250 Remington, 50 gr. Ballistic silver- tip, 222 Remington, 40 gr. Ballistic Silvertip, 223 Remington, 50 gr. Ballistic Silvertip, 243 Winchester, 55 gr. Ballistic Silvertip, 25-06 Remington, 115 gr. Ballistic Silvertip, 270

Winchester, 130 gr. Ballistic Silvertip, 280 Remington, 140 gr. Ballistic Silvertip, 7mm Remington Magnum, 150 gr. Ballistic Silvertip, 30-06 Springfield, 150 gr. Ballistic Silvertip, 30-06 Springfield, 168 gr. Ballistic Silvertip, 300 Winchester Magnum, 180 gr. Ballistic Silvertip, 308 Winchester, 150 gr. Ballistic Silvertip, 308 Winchester, 168 gr. Ballistic Silvertip, 338 Winchester Magnum, 200 gr. Ballistic Silvertip, 5.5 mm; 55 Grain Full Metal Jacket

CHEMICAL FAMILY: Mixture

FORMULA: Not Applicable/Mixture

USE DESCRIPTION: Centerfire rifle loaded ammunition

OSHA HAZARD CLASSIFICATION: Explosive

SECTION 2 COMPONENT DATA

PRODUCT COMPOSITION

Consists of the following four components:

COMPONENT NUMBER	PERCENT	PRODUCT	PRODUCT CODE
A) Projectile DPE.000022	30-60%	Centerfire Bullet	
B) Brass Shellcase BPE.020000	30-55%	Brass 2XXX Series	
C) Propellant DPE.090000	6-15%	Smokeless Powder	
D) Primer DPE.020000	.5-3%	Centerfire Primer	

Additional information may be obtained from Olin by requesting the MSDS for any component of interest and quoting the relevant product code number. All percent compositions specified below are based on the entire product.

A) Projectile

CAS or CHEMICAL NAME: Lead

CAS NUMBER: 7439-92-1

PERCENTAGE RANGE: 25-60%

HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)

EXPOSURE STANDARDS: See 29 CFR 1910.1025

OSHA(PEL)

ACGIH(TLV)

ppm mg/cubic-meter

ppm mg/cubic-meter

TWA: 0.05

0.15

CEILING: None

None

STEL: None

None

CAS or CHEMICAL NAME: Iron

CAS NUMBER: 7439-89-6

PERCENTAGE RANGE: 0-33%

HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)

EXPOSURE STANDARDS: As iron oxide fume

OSHA(PEL)

ACGIH(TLV)

ppm mg/cubic-meter

ppm mg/cubic-meter

TWA: 10

5

CEILING: None

None

STEL: None

None

CAS or CHEMICAL NAME: Copper

CAS NUMBER: 7440-50-8
PERCENTAGE RANGE: 0-20%
HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)
EXPOSURE STANDARDS:
OSHA(PEL) ACGIH(TLV)
ppm mg/cubic-meter ppm mg/cubic-meter
TWA: 1 1
CEILING: None None
STEL: None None

CAS or CHEMICAL NAME: Zinc
CAS NUMBER: 7440-66-6
PERCENTAGE RANGE: 0-3.5%
HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)
EXPOSURE STANDARDS: As zinc oxide
OSHA(PEL) ACGIH(TLV)
ppm mg/cubic-meter ppm mg/cubic-meter
TWA: 5 (respirable), 10 (total) 10
CEILING: None None
STEL: None None

CAS or CHEMICAL NAME: Aluminum
CAS NUMBER: 7429-90-5
PERCENTAGE RANGE: 0-3.5%
HAZARDOUS PER 29 CFR 1910.1200: Yes (as dust or fume)
EXPOSURE STANDARDS:
OSHA(PEL) ACGIH(TLV)
ppm mg/cubic-meter ppm mg/cubic-meter
TWA: 5 (respirable), 15 (total) 10
CEILING: None None
STEL: None None

CAS or CHEMICAL NAME: Antimony
CAS NUMBER: 7440-36-0
PERCENTAGE RANGE: 0.1-1.5%
HAZARDOUS PER 29 CFR 1910.1200: Yes
EXPOSURE STANDARDS:
OSHA(PEL) ACGIH(TLV)
ppm mg/cubic-meter ppm mg/cubic-meter
TWA: 0.5 0.5
CEILING: None None
STEL: None None

B) Brass Shellcase

CAS or CHEMICAL NAME: Copper (See above)
CAS NUMBER: 7440-50-8
PERCENTAGE RANGE: 25-40%

CAS or CHEMICAL NAME: Zinc (See above)
CAS NUMBER: 7440-66-6
PERCENTAGE RANGE: 13-17%

C) Propellant

CAS or CHEMICAL NAME: Nitrocellulose
CAS NUMBER: 9004-70-0
PERCENTAGE RANGE: 7-12%
HAZARDOUS PER 29 CFR 1910.1200: Yes

EXPOSURE STANDARDS: None Established

CAS or CHEMICAL NAME: Nitroglycerin

CAS NUMBER: 55-63-0

PERCENTAGE RANGE: .5-2%

HAZARDOUS PER 29 CFR 1910.1200: Yes

EXPOSURE STANDARDS:

OSHA (PEL)		ACGIH (TLV)	
ppm	mg/cubic-meter	ppm	mg/cubic-meter
TWA:	0.1 (skin)		0.05 (skin)
CEILING:	None		None
STEL:	None		None

CAS or CHEMICAL NAME: Dibutyl phthalate

CAS NUMBER: 84-74-2

PERCENTAGE RANGE: .5-2%

HAZARDOUS PER 29 CFR 1910.1200: Yes

EXPOSURE STANDARDS:

OSHA (PEL)		ACGIH (TLV)	
ppm	mg/cubic-meter	ppm	mg/cubic-meter
TWA:	5		5
CEILING:	None		None
STEL:	None		None

D) Primer

CAS or CHEMICAL NAME: Copper (See above)

CAS NUMBER: 7440-50-8

PERCENTAGE RANGE: 0.5-2%

CAS or CHEMICAL NAME: Zinc (See above)

CAS NUMBER: 7440-66-6

PERCENTAGE RANGE: 0.1-1%

CAS or CHEMICAL NAME: Lead styphnate

CAS NUMBER: 15245-44-0

PERCENTAGE RANGE: 0.1-1%

HAZARDOUS PER 29 CFR 1910.1200: Yes

EXPOSURE STANDARDS: See lead (above)

CAS or CHEMICAL NAME: Barium nitrate

CAS NUMBER: 10022-31-8

PERCENTAGE RANGE: 0.1-1%

HAZARDOUS PER 29 CFR 1910.1200: Yes

EXPOSURE STANDARDS:

OSHA (PEL)		ACGIH (TLV)	
ppm	mg/cubic-meter	ppm	mg/cubic-meter
TWA:	0.5		0.5
CEILING:	None		None
STEL:	None		None

SECTION 3 PRECAUTIONS FOR SAFE HANDLING AND STORAGE

DO NOT TAKE INTERNALLY. AVOID CONTACT WITH SKIN, EYES AND CLOTHING.
UPON CONTACT WITH SKIN OR EYES, WASH OFF WITH WATER.

STORAGE CONDITIONS: STORE IN A COOL, DRY, WELL VENTILATED PLACE, AWAY FROM ALL SOURCES OF IGNITION DO NOT STORE AT TEMPERATURES ABOVE: Not Applicable

DO NOT SUBJECT TO MECHANICAL SHOCK.

PRODUCT STABILITY AND COMPATIBILITY

SHELF LIFE LIMITATIONS: 25-30 Years

INCOMPATIBLE MATERIALS FOR STORAGE OR TRANSPORT: Acids, Class A & B explosives, Strong oxidizers, and Caustics.

SECTION 4 PHYSICAL DATA

APPEARANCE: Cylindrical, brass cartridge

FREEZING POINT: Not Applicable

BOILING POINT: Not Applicable

DECOMPOSITION TEMPERATURE: Not Applicable

SPECIFIC GRAVITY: Not Applicable

BULK DENSITY: Not Applicable

pH @ 25 DEG.C: Not Applicable

VAPOR PRESSURE @ 25 DEG.C: Not Applicable

SOLUBILITY IN WATER: Not Applicable

VOLATILES, PERCENT BY VOLUME: Not Applicable

EVAPORATION RATE: Not Applicable

VAPOR DENSITY: Not Applicable

MOLECULAR WEIGHT: Not Applicable

ODOR: None

COEFFICIENT OF OIL/WATER DISTRIBUTION: Not Applicable

SECTION 5 PERSONAL PROTECTIVE EQUIPMENT REQUIREMENTS

PERSONAL PROTECTION FOR ROUTINE USE OF PRODUCT:

RESPIRATORY PROTECTION: If air concentrations above the TLV are possible, wear a NIOSH approved respirator.

VENTILATION: Local exhaust ventilation is recommended if significant dusting occurs. Otherwise, use general exhaust ventilation. Use explosion-proof ventilation.

SKIN AND EYE PROTECTIVE EQUIPMENT: Use safety glasses.

EQUIPMENT SPECIFICATIONS (WHEN APPLICABLE):

RESPIRATOR TYPE: NIOSH approved HEPA filter respirator.

PROTECTIVE CLOTHING TYPE (This includes: gloves, boots, apron, protective suit): Not normally needed.

SECTION 6 FIRE AND EXPLOSION HAZARD INFORMATION

FLAMMABILITY DATA:

EXPLOSIVE: Yes

FLAMMABLE: Not Applicable

COMBUSTIBLE: Not Applicable

PYROPHORIC: No

FLASH POINT: Not Applicable

AUTOIGNITION TEMPERATURE: No Data

FLAMMABLE LIMITS AT NORMAL ATMOSPHERIC TEMPERATURE AND PRESSURE
(PERCENT VOLUME IN AIR): LEL - Not Applicable UEL - Not Applicable

NFPA RATINGS: Not Established

HMIS RATINGS:

Health:	0
Flammability:	2
Reactivity:	4

EXTINGUISHING MEDIA: Floor area with water, if no water is available, use carbon dioxide, dry chemical or earth. If the fire reaches the cargo withdraw and let fire burn.

FIRE FIGHTING TECHNIQUES AND COMMENTS: See Section 11 for protective equipment for fire fighting.

OTHER: If fire reaches cargo, do not fight, evacuate all persons, including emergency responders from the area for 1500 feet (1/3 mile) in all directions.

SECTION 7 REACTIVITY INFORMATION

CONDITIONS UNDER WHICH THIS PRODUCT MAY BE UNSTABLE:

TEMPERATURES ABOVE: No Data

MECHANICAL SHOCK OR IMPACT: Yes (based on primer)

ELECTRICAL (STATIC) DISCHARGE: Yes (based on primer)

OTHER: CARTRIDGE MAY DETONATE IF CASE IS PUNCTURED OR SEVERELY DAMAGED

HAZARDOUS POLYMERIZATION: Will not occur

INCOMPATIBLE MATERIALS: Strong acids and caustics

HAZARDOUS DECOMPOSITION PRODUCTS: Nitrogen oxides, carbon monoxide, lead oxides, carbon dioxide, lead dust/fume

SUMMARY OF REACTIVITY:

EXPLOSIVE:	Yes
OXIDIZER:	No
PYROPHORIC:	No
ORGANIC PEROXIDE:	No
WATER REACTIVE:	No

SECTION 8 FIRST AID

EYES: Not a likely route of exposure.

SKIN: Not a likely route of exposure.

INGESTION: Not a likely route of exposure.

INHALATION: Not a likely route of exposure.

SECTION 9 TOXICOLOGY AND HEALTH INFORMATION

ROUTES OF ABSORPTION

The physical nature of this product makes absorption from any route unlikely. A small amount of inhalable particles may be created when projectile is fired.

WARNING STATEMENTS AND WARNING PROPERTIES

PARTICLES FROM FIRING MAY BE HARMFUL IF INHALED.

HUMAN THRESHOLD RESPONSE DATA

ODOR THRESHOLD: No available data

IRRITATION THRESHOLD: No available data

IMMEDIATELY DANGEROUS TO LIFE OR HEALTH: The IDLH concentration has not been established.

SIGNS, SYMPTOMS, AND EFFECTS OF EXPOSURE

INHALATION

ACUTE: Inhalation of lead dust or metal fume may cause irritation to nose, throat, upper respiratory tract and lung. The irritant effects may lead to bronchitis, headache, a fall in blood pressure, weakness, convulsions and collapse may occur. Severe poisoning may impair vision by damaging the optic nerve. The product is composed of a solid projectile. It is judged that the physical nature of the product, and its use would preclude inhalation of a sufficient amount of lead and the development of these symptoms.

CHRONIC: Chronic inhalation of lead dust or metal fume may cause damage to central and peripheral nerves, blood, kidneys, and the fetus. Male reproductive function may be impaired. Damage to nerves can result in reduction in motor nerve and muscle function. Anemia may result due to interference by lead of hemoglobin synthesis. Lead has been identified as an animal carcinogen; it may produce cancer in humans. Chronic exposure may lead to lead poisoning, known as "plumbism", causing gingival lead line and an accumulation in body tissues. The product is composed of a solid projectile. It is judged that the physical nature of the product, and its use would preclude inhalation of a sufficient amount of lead and the development of these symptoms.

SKIN

ACUTE: Lead can be absorbed through the skin to produce effects similar to those listed for acute inhalation exposure.

CHRONIC: Lead can be absorbed through the skin to produce effects similar to those listed under chronic inhalation exposure. The product is composed of a solid projectile. It is judged that the physical nature of the product, and its use would preclude skin absorption of a sufficient amount of lead and the development of these acute and/or chronic symptoms.

EYE

Lead dust and fume can irritate the eyes with conjunctival redness and discharge. It is judged that this effect would not occur because of the physical nature of the product and its use.

INGESTION

ACUTE: The effects of lead ingestion would be similar to those listed under acute inhalation exposure in addition to gastrointestinal tract irritation.

CHRONIC: The effects of lead ingestion would be similar to those listed under chronic inhalation exposure. The product is composed of a solid projectile. It is judged that the physical nature of the product, and its use would preclude ingestion and the development of these acute and/or chronic symptoms.

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE

Exposure to lead can aggravate anemia, cardiovascular and respiratory disease. There are no medical conditions known to be aggravated by exposure to this product, due to its physical nature and use.

INTERACTIONS WITH OTHER CHEMICALS WHICH ENHANCE TOXICITY

There are no chemicals known to enhance the toxicity of the product.

ANIMAL TOXICOLOGY

ACUTE TOXICITY:

Inhalation LC 50: No available data

Dermal LD 50: No available data

Oral LD 50: No available data

Irritation: Not a skin or eye irritant

ACUTE TARGET ORGAN TOXICITY: Lead dust and fume can cause damage to central nervous system, blood, lungs and eyes. Nitroglycerin will produce dilation of blood vessels and drop in blood pressure, which may affect the heart. It has also been shown to cause methemoglobinemia (cyanosis). It is judged that the low concentration of nitroglycerin and the physical nature of the product would preclude the occurrence of these symptoms from exposure to this product. Ingestion of large doses of soluble barium compounds can cause cyanosis, skeletal muscle paralysis, respiratory arrest, irregular heartbeat and hypertension. This product is composed of a finished cartridge and the primer is completely sealed. Ingestion of the product in its final form is unlikely. If inhaled, zinc fume can cause an influenza type reaction known as metal fume fever. Symptoms of this reaction may include metallic taste, runny nose, nausea, fever and chills. These effects usually disappear after 24 hours. It is judged that the physical nature of the product, the low percentage of zinc in the product, and its use would preclude the development of metal fume fever.

CHRONIC TARGET ORGAN TOXICITY: Inhalation of lead can cause damage to the blood, central and peripheral nervous systems and kidney. Lead inhibits the production of hemoglobin, the material in the blood, which carries oxygen. Anemia may result. Lead also causes damage to peripheral nerves resulting in a decrease in motor nerve and muscle function. The product is composed of a solid projectile. It is judged that the physical nature of the product and its use would preclude the development of these effects. Inhalation of iron dust or fumes has been shown to cause a benign pneumoconiosis known as siderosis. This condition is characterized by deposition of iron in the lungs without subsequent fibrotic changes or impairment of lung function. The physical nature of the product, the low percentage of iron in the product, and its use would preclude the development of siderosis. Inhalation of aluminum dust or fume has produced lung fibrosis in laboratory animals. It is judged that the physical nature of the product, the low percentage of aluminum in the product, and its use would preclude the development of lung fibrosis.

REPRODUCTIVE AND DEVELOPMENTAL TOXICITY:

Lead has been shown to affect fetal development and reduce male reproductive function. Lead crosses the placenta and may affect the fetus causing birth defects, mental retardation, behavioral disorders, and death during the first year of childhood. The product is composed of a solid projectile. It is judged that the physical nature and use of the product would preclude the development of these effects.

CARCINOGENICITY:

This product is not known or reported to be carcinogenic by any

reference source including IARC, OSHA, NTP or EPA. Lead is classified as a carcinogen by IARC. Based on the physical nature of the product and its use, it is judged that the risk of cancer is not significant from exposure to the product.

MUTAGENICITY:

This product is not known or reported to be mutagenic.

AQUATIC TOXICITY:

The LC 50 of lead (48 hrs.) to bluegill (*Lepomis macrochirus*) is reported to be 2-5 mg/l. Fish are unaffected by nitrocellulose at concentrations of 1000 mg/l.

Barium Nitrate:

The lethal concentration of barium nitrate toward stickleback at 15-18 Deg.C has been reported as 400 mg/l as barium, or 760 mg/l as barium nitrate. The average survival times for higher concentrations were one week at 500 mg/l, four days at 1000 mg/l, two days at 2500 mg/l, and only one day at 3000 mg/l, all as barium. It has been found that the maximum concentration of barium nitrate that did not affect fish was 25 mg/l. In Lake Huron water at 12 Deg.C, 5 mg/l had no effect on rainbow trout, bluegill sunfish, or the sea lamprey during a 24-hour exposure.

SECTION 10 TRANSPORTATION INFORMATION

THIS MATERIAL IS REGULATED AS A DOT HAZARDOUS MATERIAL.

DOT DESCRIPTION FROM THE HAZARDOUS MATERIALS TABLE 49 CFR 172.101:

LAND (U.S. DOT): CARTRIDGES, SMALL ARMS (OTHER THAN BLANKS), 1.4S, UN0012, PG II

WATER (IMO): SAME AS ABOVE

AIR (IATA/ICAO): SAME AS ABOVE

HAZARD LABEL/PLACARD: NONE REQUIRED

REPORTABLE QUANTITY: NOT APPLICABLE (Per 49 CFR 172.101, Appendix)

EMERGENCY GUIDE NO: 114

SPECIAL COMMENTS: May be reclassified domestically as an ORM-D if appropriately packaged per 49 CFR 173.230.

SECTION 11 SPILL AND LEAKAGE PROCEDURES

FOR ALL TRANSPORTATION ACCIDENTS, CALL CHEMTREC AT 800-424-9300.

REPORTABLE QUANTITY: (Per 40 CFR 302.4) as nitroglycerine 10 lbs., dibutyl phthalate 10 lbs., antimony 5000 lbs.

SPILL MITIGATION PROCEDURES:

Evacuation procedures must be placed into effect. Evacuate all non-essential personnel. Hazardous concentrations in air may be found in local spill area and immediately downwind. This product does represent an explosion hazard from heat, shock, friction, static discharge, etc. Remove all sources of ignition. Stop source of spill as soon as possible and notify appropriate personnel.

AIR RELEASE: Not Applicable

WATER RELEASE: Handle as described in land spill.

LAND SPILL: Do not place spill materials back in their original containers. Containerize and label all spill materials properly. Decontaminate all clothing and the spill area using soap solution and flush with large amounts of water. Evacuate all non-essential personnel, shut off all ignition sources, no flames, smoking or flames in hazard area.

SPILL RESIDUES:

Dispose of per guidelines under Section 12, WASTE DISPOSAL.

PERSONAL PROTECTION FOR EMERGENCY SPILL AND FIRE-FIGHTING SITUATIONS:

No extra protection required beyond that listed in Section 5 (In case of fire, use normal fire fighting equipment). Protection concerns must also address the potential of the physical characteristic of this product as explosive.

SECTION 12 WASTE DISPOSAL

If this product becomes a waste, it meets the criteria of a hazardous waste as defined under 40 CFR 261 and would have the following EPA hazardous waste number: D003.

If this product becomes a waste, it will be a hazardous waste, which is subject to the Land Disposal Restrictions under 40 CFR 268 and must be managed accordingly.

OTHER: Deactivation

CARE MUST BE TAKEN TO PREVENT ENVIRONMENTAL CONTAMINATION FROM THE USE OF THIS MATERIAL. THE USER OF THIS MATERIAL HAS THE RESPONSIBILITY TO DISPOSE OF UNUSED MATERIAL, RESIDUES AND CONTAINERS IN COMPLIANCE WITH ALL RELEVANT LOCAL, STATE AND FEDERAL LAWS AND REGULATIONS REGARDING TREATMENT, STORAGE AND DISPOSAL FOR HAZARDOUS AND NONHAZARDOUS WASTES.

SECTION 13 ADDITIONAL REGULATORY STATUS INFORMATION

TOXIC SUBSTANCES CONTROL ACT:

The components of this product are listed on the Toxic Substance Control Act inventory.

CALIFORNIA SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986 - PROPOSITION 65:

"WARNING: This product contains detectable amounts of a chemical(s) known to the State of California to cause cancer and/or birth defects or other reproductive harm."

SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT TITLE III:

HAZARD CATEGORIES, PER 40 CFR 370.2:

HEALTH: None

PHYSICAL: Sudden release of pressure

EMERGENCY PLANNING AND COMMUNITY RIGHT TO KNOW, PER 40 CFR 355, APP.A:

EXTREMELY HAZARDOUS SUBSTANCE - THRESHOLD PLANNING QUANTITY: None
Established

SUPPLIER NOTIFICATION REQUIREMENTS, PER 40 CFR 372.45: None Established

SECTION 14 ADDITIONAL INFORMATION

MSDS REVISION STATUS: Synonyms revised

SECTION 15 MAJOR REFERENCES

1. Friberg, L., G.F. Nordberg, and V.B. Vouk, eds., Handbook on the Toxicology of Metals, Vol. II, Elsevier, New York, 1986.
2. Lee, Cheng-Chun, et al., Mammalian Toxicity of Munition Compounds: Phase I. Acute Oral Toxicity, Primary Skin and Eye Irritation, Dermal Sensitization, and Disposition and Metabolism. NTIS Report (ADB011150), National Technical Information Services, Springfield, VA. Report No. 1, July 22, 1975.

* Other References are available upon request.

THIS MATERIAL SAFETY DATA SHEET (MSDS) HAS BEEN PREPARED IN COMPLIANCE WITH THE FEDERAL OSHA HAZARD COMMUNICATION STANDARD, 29 CFR 1910.1200. THE INFORMATION IN THIS MSDS SHOULD BE PROVIDED TO ALL WHO WILL USE, HANDLE, STORE, TRANSPORT, OR OTHERWISE BE EXPOSED TO THIS PRODUCT. THIS INFORMATION HAS BEEN PREPARED FOR THE GUIDANCE OF PLANT ENGINEERING, OPERATIONS AND MANAGEMENT AND FOR PERSONS WORKING WITH OR HANDLING THIS PRODUCT. OLIN BELIEVES THIS INFORMATION TO BE RELIABLE AND UP TO DATE AS OF THE DATE OF PUBLICATION, BUT MAKES NO WARRANTY THAT IT IS. ADDITIONALLY, IF THIS MSDS IS MORE THAN THREE YEARS OLD, YOU SHOULD CONTACT OUR CORPORATE DIRECTOR: ENVIRONMENT, HEALTH AND SAFETY AT THE PHONE NUMBER ON THE FRONT PAGE TO MAKE CERTAIN THAT THIS DOCUMENT IS CURRENT.

OLIN CORPORATION

501 Merritt 7
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APPENDIX K

When Unused Military Munitions Become Waste Military Munitions (Chapter 4 of DoD Policy Guidance)

A. General. Unused military munitions include those that have not been fired, dropped, launched, placed, or otherwise used. Examples include military munitions that are:

1. In the active inventory that are available for issue and use in training or operations.
2. Issued to a using unit, but were not used and will be returned to storage. (This includes unused military munitions recovered from amnesty boxes.)
3. Rejected during the manufacturing process or prior to use. (Note: This example can include rejected munitions and residues that meet the definition of a military munition in Chapter 2.)

B. Military munitions become waste under any of the conditions indicated below. (Figure 1 provides a flowchart of this process.) When the military munitions are:

1. Declared a Waste by an Authorized Military Official (AMO). (Note: Although the MR states that an AMO can declare a military munition to be waste, DoD limits the AMO's authority to designating entire classes of munitions as waste.)

2. Abandoned by being disposed of by being: buried, landfilled, or dumped at sea; burned; detonated, the exception is when detonated as a consequence of intended use; incinerated; or treated prior to disposal. This MR provision is a factual determination that is not dependent on a DDA's or AMO's specific declaration as a WMM. Specific examples of munitions that become a waste under this provision of the MR include:

- a. Open burning or open detonation (OB/OD) that is not conducted as part of emergency response activities or training.

- b. Incineration of munitions.

- c. Burial of unused munitions as a field expedient means of disposal. (This practice is strictly prohibited.) The buried military munition becomes a waste at the time of burial.

3. Removed from a Storage Facility for Disposal or Treatment Prior to Disposal (Igloo Door Rule). Military munitions in storage that have not been declared WMM become WMM when removed from storage for the purpose of disposal or treatment prior to disposal. (This includes military munitions shipped to another installation for the purpose of disposal or treatment prior to disposal.) Once removed from storage for disposal or treatment prior to disposal, these munitions must be transported, stored, or managed as WMM.

4. **Damaged or Deteriorated.** Military munitions that are damaged or deteriorated to a point they cannot be made serviceable or recycled for other purposes are WMM. Munitions custodians will conduct a preliminary evaluation of damaged or deteriorated military munitions through either visual inspection or a more in-depth surveillance and report the condition to the Item Manager or the inventory management official and the DDA, as appropriate. If the Item Manager or inventory management official determines that the munitions cannot be returned to serviceable condition or used for another purpose, they must coordinate this determination with and request disposition instructions from the appropriate DDA. This waste determination must be completed within the time constraint allowed for the DDA evaluation process in Chapter 6.

a. **Emergency Response.** If the munitions custodian finds the military munition is damaged or deteriorated to the point it poses a potential explosives safety hazard, the munition will be handled per Chapter 9 of this policy.

b. **Emergency Destruction.** Munitions become WMM immediately upon issuance of a Notice of Ammunition Reclassification (NAR), Ammunition Information Notice (AIN), Technical Order (TO), or similar document that requires treatment of the item within 60 days and states that after 60 days the item presents a safety hazard for handling, transportation, or continued storage. (A munition item that fails stability testing is an example of such.)

(1) Item or Program Managers must coordinate the issuance of this type of NAR, AIN, or TO with the DoD Component DDA prior to its issuance.

(2) The local installation will contact the applicable Component DDA immediately upon receipt of a NAR, or similar document, for disposition instructions. Munitions identified in such documents (e.g., NARs, AINs, TOs and etc.) should be given highest priority for treatment in a RCRA permitted or interim status unit.

(3) If treatment in a RCRA permitted or interim status unit cannot be conducted within the time frame directed in the NAR, AIN, or TO, or the item is unsafe to transport, the installation or responsible activity commander will request a RCRA emergency permit allowing treatment from the EPA or State regulatory agency. Request for an emergency permit is authorized only after all efforts have been exhausted through the process described in paragraph (2) above.

APPENDIX L
When Used Military Munitions Become Waste Military Munitions
(Chapter 5 of DoD Policy Document)

A. General. Used or fired munitions include:

1. Military munitions that have been fired, dropped, launched, projected, placed, or otherwise used.
2. Military munitions that, when used as intended, malfunction, or misfire (e.g., fail to fire or detonate).
3. Munitions fragments, such as shrapnel, casings, fins, and other components, such as arming wires and pins, that result from the use of military munitions.

B. Used military munitions become WMM under any of the circumstances indicated below. (Figure 1 provides a flowchart of this information.)

1. **Transport Off-Range.** Used military munitions that are transported off range or from the site of use, when the site of use is not a range, for reclamation, treatment, disposal or for storage prior to reclamation, treatment or disposal are WMM. Used munitions transported off-range to be repaired or reused or that undergo additional evaluation (e.g., testing for RDT&E purposes, malfunction or misfire investigations, and evaluation of possible repair or reuse) are not waste, but may become waste after the required evaluation is completed.

2. **Recovered, Collected, and then Disposed of by Burial, or Landfill.** Used military munitions that are recovered and subsequently buried or landfilled, at any location, are WMM. (Used military munitions that were buried, at any time, became waste immediately upon burial.) Under this Policy, the burial or landfill of used munitions is permissible only when done in full compliance with DoD regulations and applicable Federal, State, or local environmental regulations.

3. **Used or Fired Munitions Landing Off-Range.** Under the MR, military munitions that as a result of use land off-range become WMM if not promptly rendered safe or retrieved. (The "promptness" of an action is situationally dependent and will require a thorough analysis of the threat to human health and the environment.)

a. Upon notification a used munition has landed off-range, the responsible DoD Component personnel will take immediate action to assess the extent and nature of the threat to human health and the environment and to conduct an appropriate response. Response actions may include destruction on site, render-safe and removal to storage for either evaluation or temporary storage prior to destruction, or transport for immediate destruction.

b. Should the munition not be able to be rendered safe, retrieved, or destroyed, it becomes WMM. When this occurs the installation or responsible activity commander responsible for range operations will maintain a record of the event until the munition item is recovered or destroyed. At a minimum, the record will include:

(1) The date the munition was fired off-range or the date the installation or responsible activity commander became aware that a munition was fired off-range.

(2) The type and quantity of munitions fired off-range.

(3) The location of the munition (if the exact location is unknown, the area where the munitions are believed to be located).

(4) The date and nature of the response actions taken.

(5) The nature of any remaining threat, including an estimate of how long that threat will remain.

C. Management of Used or Fired Munitions.

1. Until inspected and certified as containing no items of a dangerous nature (e.g., explosives), all used military munitions, to include residue (e.g., cartridge cases, shrapnel, misfires or malfunctions) from used military munitions, will be considered explosive material.

2. When demilitarization is required, it must be performed per item specific technical guidance (e.g., DMWRs, LOIs, TOs, TMs, TBs, instructions, and etc.) provided by the responsible engineering proponent and inspected and certified, by qualified personnel, as being free of explosives and releasable to the general public.

3. The flashing, crushing, or shredding of used munitions on the range (at the site of use) is an integral part of range clearance activities and are exempt from RCRA regulation. These activities may, however, be subject to other Federal, State, or local environmental regulations.

4. The commingling of used or fired munitions and non-munitions materials is not permitted.

APPENDIX M
Designated Disposition Authority (DDA) Evaluation Process
(Chapter 6 of DoD Policy Document)

A. The Evaluation Process For Determining When Military Munitions Become WMM:

1. Most military munitions will not be considered WMM without a specific DoD DDA's or Component DDA's designation as such. (In rare cases, the AMO may declare an entire class of munitions as WMM.) However, in limited circumstances, local, qualified munitions handlers are authorized to classify a munition as a WMM. These involve MR provisions that define a munition as waste without a specific designation by a DoD Component DDA or DoD DDA and include:

a. An unused munition that is abandoned by being disposed of by burial; burned; detonated, the exception is when detonated as a consequence of intended use; incinerated; or treated prior to disposal.

b. A used munition that is:

(1) Transported off a range or from the site of use for the purposes of reclamation, treatment, disposal, or storage prior to or instead of reclamation, treatment, or disposal.

(2) Recovered, collected, and then disposed of by burial, or landfill either on or off a range.

c. Ammunition that lands off range and is not promptly destroyed in place rendered safe or retrieved.

2. Local Authorization to Treat WMM:

a. Unused WMM. Except in the case of an explosives or munitions emergency, installations are not authorized to treat or dispose of unused military munitions without prior DDA approval.

b. Used or Fired WMM. Used munitions that are classified as WMM must be managed as waste per RCRA and this policy. (See Chapter 7.)

3. Designated Disposition Authority (DDA). (Figure 2 provides DDA points of contact.)

a. Authority to Designate Munitions as a Waste. DDA's are the only personnel authorized to declare unused military munitions as WMM, the exceptions are explosives or munitions emergencies, abandoned (e.g., buried) munitions, or an AMO's declaration of a class of munitions as WMM. DDAs will declare munitions to be WMM in the following circumstances:

(1) When the unused military munition is removed from storage for disposal or treatment prior to disposal.

(2) When the unused military munition is damaged or deteriorated to the point it cannot be returned to serviceable condition and cannot reasonably be recycled or used for other purposes. (This includes emergency destruction as described in Chapter 4.)

(3) When a used munitions is involved in a misfire or malfunction investigation and cannot be returned to serviceable condition.

b. DDA Evaluation Considerations. DDAs will maintain records documenting the evaluation used prior to the DDA's issuance of disposition instructions. As part of their evaluation, DDA will consider:

(1) Safety. (See Chapter 9 for emergency responses.)

(2) Use for Intended Purpose. Prior to directing demilitarization, DDAs will consider opportunities (e.g., training or selling, to include consideration for Foreign Military Sales or RDT&E) that would prevent the need for demilitarization.

(3) Resource Recovery and Recycling (R3). DDA's will determine whether munition items scheduled for demilitarization can be processed through R3, prior to declaring them WMM. Unused military munitions processed through R3 are not WMM.

(4) Treatment and Disposal. The DDA will consider the availability and location of treatment facilities.

c. DDA Disposition Instructions. When the DDA declares munitions as WMM, the DDA must provide the installation or responsible activity specific instructions for either local treatment (if the local installation has a RCRA permitted or interim status treatment unit) or for the timely shipment of the WMM to a DoD Component, SMCA or commercial treatment facility.

d. Unique Accountability Identifier. For consistency and to provide visibility of WMM in existing munitions management systems, the Joint Ordnance Commanders Group (JOCG) has requested the Defense Logistics Agency (DLA) assign WMM a unique Condition Code identifier. Until DLA assigns WMM a new Condition Code, installations and responsible activities will use a Disposal Authority Code (DAC) of M to identify WMM.

B. DDA Disposition Process.

1. Local Activity Request for Disposition. Local activities will request disposition when it determines the munitions are excess or unusable at the local level. Local activities will request disposition instructions from the appropriate DoD Component DDA (see Figure 2) and coordinate this request with the item manager as appropriate. Disposition requests should include the following:

a. Statement, if known, of other uses (e.g., training) for these munitions.

b. If applicable, an explanation of the circumstances, to include the date, under which the munitions were classified as WMM (e.g., emergency destruction and buried munitions).

c. A statement regarding the regulatory status (e.g., conditionally exempt storage, less than 90-day storage, or permitted or interim status storage) of the WMM storage facility. (See Chapter 7, Section C.)

d. Statement regarding the availability or non-availability of RCRA-interim status or RCRA-permitted hazardous waste treatment or disposal units located on the installation.

2. DoD Component or DoD DDA will:

a. Maintain accountability of all disposition requests and be able to provide status of evaluation upon request.

b. Evaluate the munitions and document the evaluation. (See paragraph A3b of this chapter.)

c. Provide disposition instructions within 60 days. When the DoD Component DDA must subsequently request disposition instructions from the DoD DDA, the DoD Component DDA will advise the local activity that the request has been forwarded.

3. DDA disposition instructions will include:

a. Instructions for application of the WMM accountability identifier, if applicable.

b. The date the military munitions were designated as WMM, if applicable.

(1) For munitions that automatically became a waste (e.g., buried unused munitions), the date of the action that made them waste will be used.

(2) For munitions that become a waste upon removal from storage for treatment or disposal, the disposition instructions will state that the military munitions becomes WMM on the date it is removed from storage for treatment or disposal.

(3) For damaged or deteriorated munitions, the date the DDA determined the item cannot be put into serviceable condition and cannot be recycled or used for other purposes.

(4) For all other military munitions, the date the DDA determined them to be WMM.

c. Specific Instructions:

(1) If the munitions are to be shipped off-site for treatment or disposal, disposition instructions will designate the facility to which the munitions are to be sent, the date by which shipment must occur, and the receiving installation's point of contact (POC).

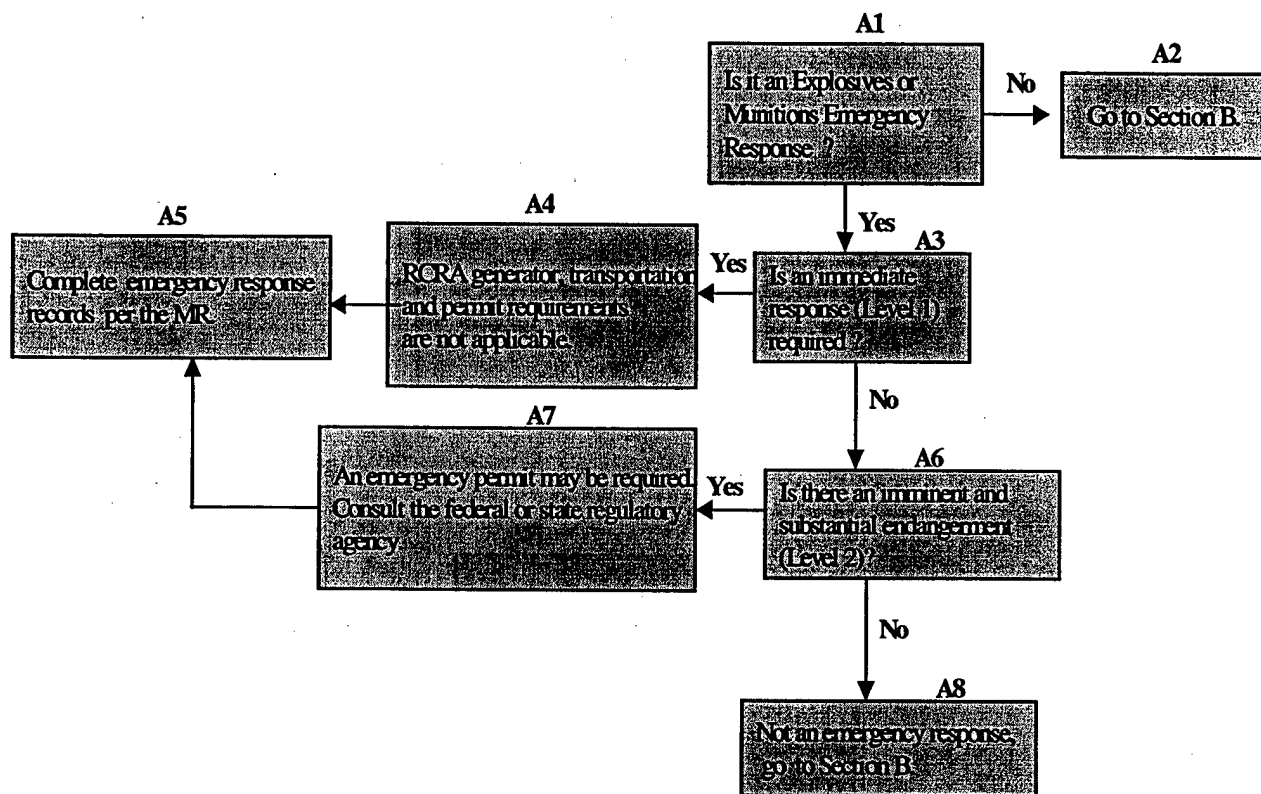
(2) DoD Component DDA's will only direct "local treatment" at installations that have a RCRA permit, an interim status treatment facility that is permitted to treat the WMM, or has been granted an emergency permit by either EPA or the State. If treatment in a RCRA permitted or interim status unit cannot be conducted within the time frame directed by the DDA or the item is unsafe to transport to a RCRA facility, the installation or responsible activity

commander will request a RCRA emergency permit from the EPA or State regulatory agency allowing treatment. (See Chapter 9, A4b for more information on emergency permits.) The term "local disposal" will no longer be used.

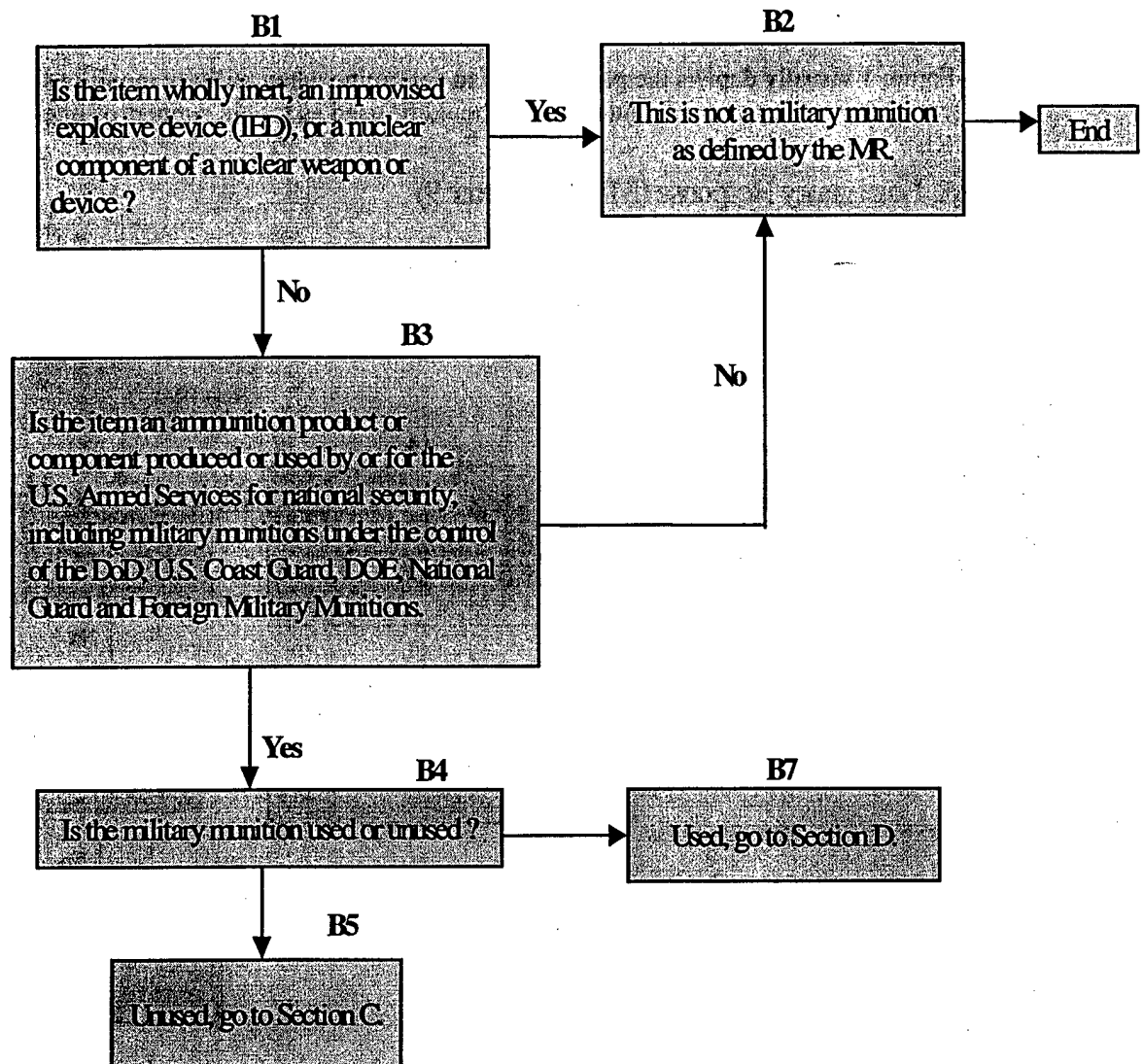
Figure 1:
MR Evaluation Process Schematic

Figure 1 visually depicts the process used to determine when military munitions become WMM. It provides general guidance and should be used as tool in support of implementing the MRIP.

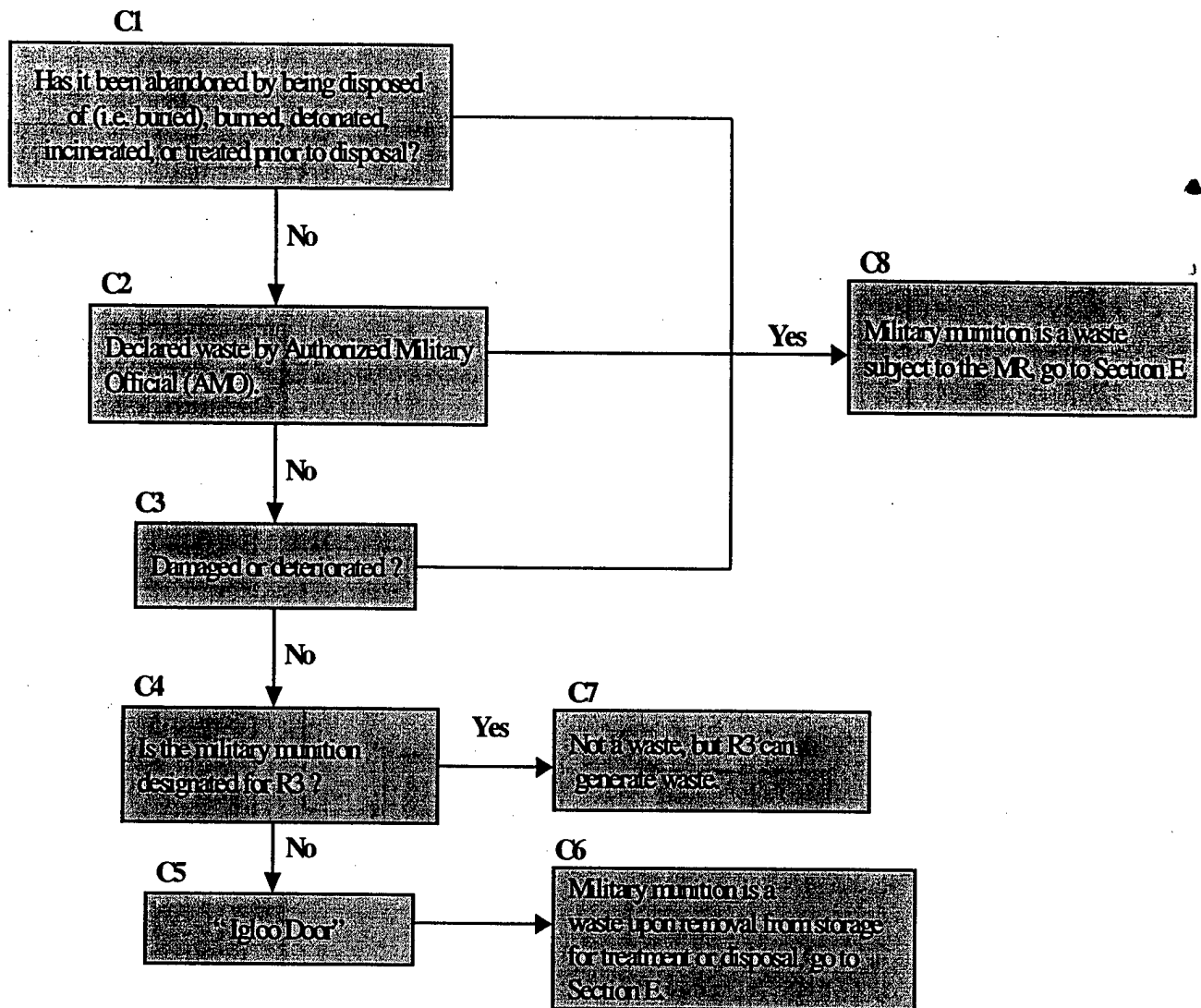
A. Emergency Response (MRIP Chapter 9)



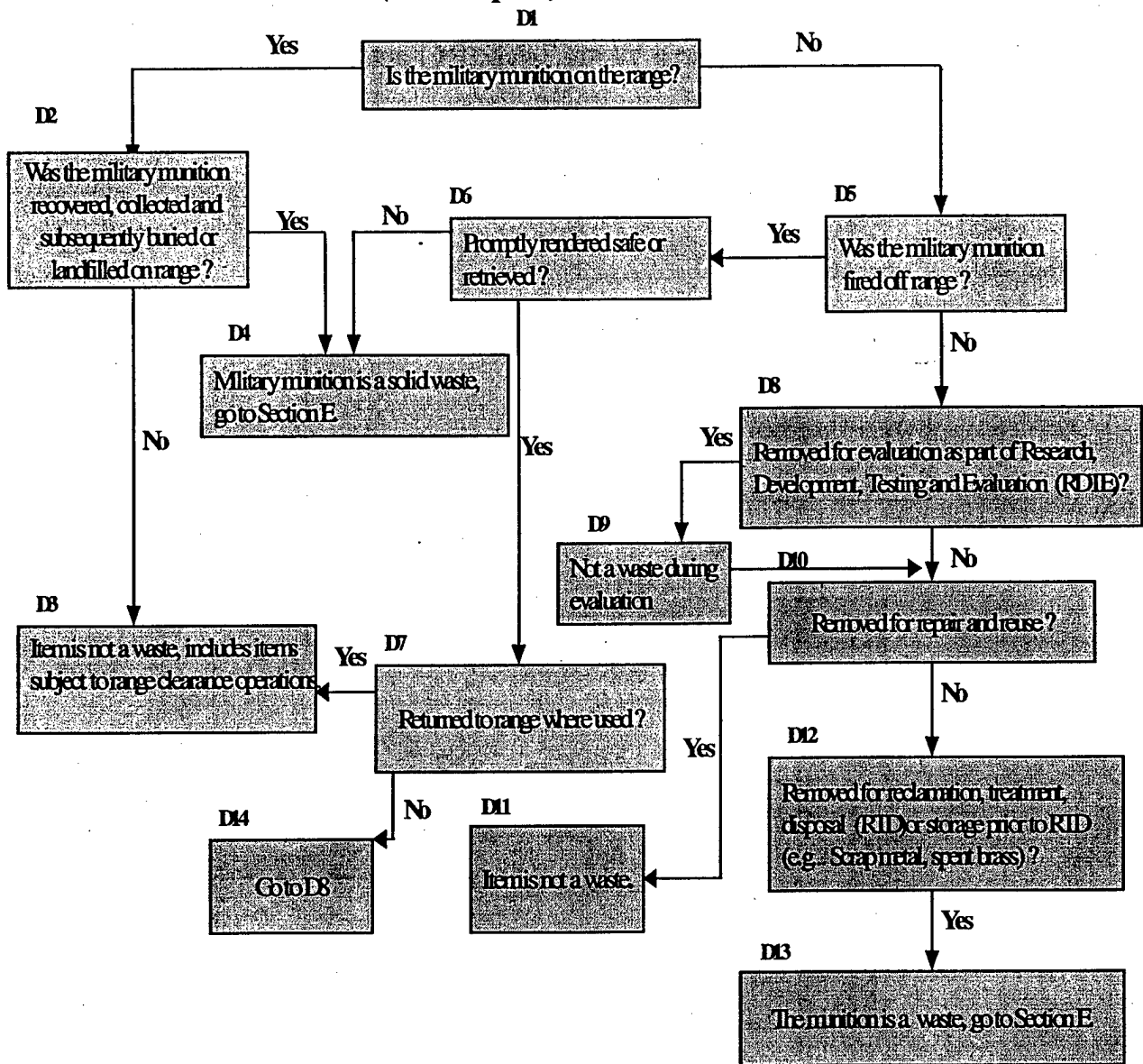
B. Is it A Military Munition ? (MRIP Chapter 2)



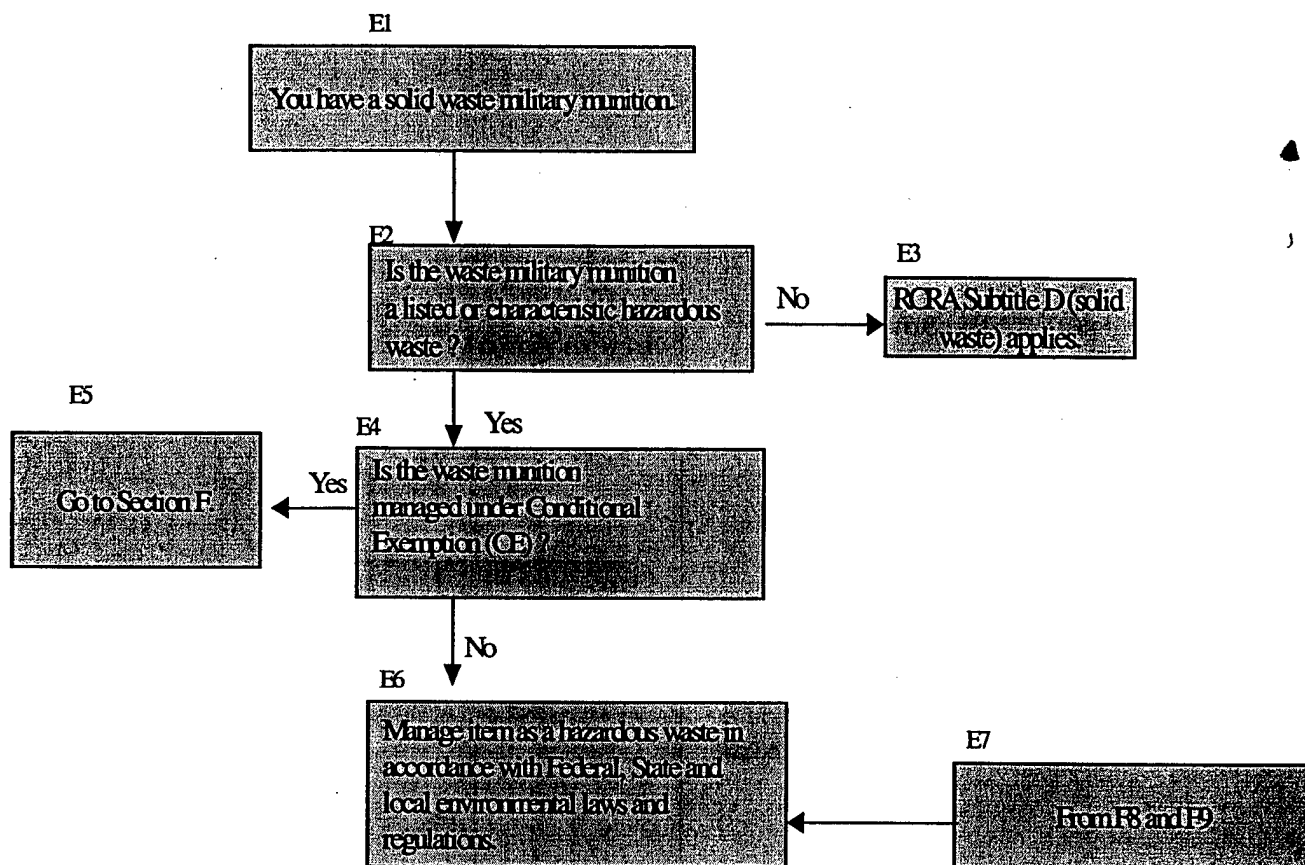
C. Is The Unused Munition a Waste ? (MRIP Chapter 4)



D Is The Used Munition a Waste ? (MRIP Chapter 5)



E. Waste Determination (MRIP Chapter 7)



F. Conditional Exemption (MRIP Chapter 7)

